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The "total" amount of sediments and the composition of the "average igneous rock"

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ABSTRACT

Assuming sediments to derive exclusively from granite-granodiorite and basalt the chemical composition of the "average igneous rock" is found to be almost identical with that of the Appalachian and Cordilleran igneous rocks as determined by A. Knopf (1916). The total amount of weathered igneous rocks is found to be 194 ± 21, the amount of shale 172 ± 28, sandstone 17·3 ± 21, limestone 12·8 ± 4·3, and dolomite 6·8 ± 3·0, all in kg per cm² earth surface. The total amount of sediments formed by complete weathering is thus 209 ± 35 in the same unit. The results and their degree of accuracy are discussed and compared with the results of previous calculations.

Introduction

One of the difficult, but at the same time important problems of quantitative geochemistry is to determine the total mass of sediments. Intimately connected with this problem is the question of how to determine the chemical composition of the average igneous rock.

A detailed review of the discussions of these problems is not necessary in this journal, and therefore readers not familiar with them are referred to standard treatises, *e.g.* Mason (1952), Kuenen (1950), Rankama and Sahama (1950), or to Correns (1948).

The problem might be formulated in the following way. If E is the total amount of weathered average igneous rock, M the total amount of sea water, S the total amount of sediments formed from igneous rocks, and e_x, m_x and s_x the weight percentages of an element (or oxide) X in each rock type the following equation will be satisfied for each element (or oxide)

$$e_x E = m_x M + s_x S \tag{1}$$

Only M and m_x are accurately known of the six quantities in equation (1). However, when accurate chemical analyses of suitable rocks from all parts of the world will be available, it will be possible to determine e_x and s_x.

The Composition of the Average Igneous Rock, and a Reformulation of the Previous Problem

For more than fifty years the composition of igneous rocks has been repeatedly discussed. Recent discussions are based mostly on the classic paper by Clarke and Washington (1924), which is the final version of earlier papers by Clarke, and which is based on the big compilation of superior rock analyses previously prepared by Washington (1917). They used the arithmetic mean of all the rock analyses tabulated in Washington's compilation. The validity of this method has been repeatedly discussed and most critics have pointed out that a calculation must be based on the frequencies of all the different rock types. Some of them have estimated the chemical composition of selected areas (Knopf, 1916; Sederholm, 1925;

GROUT, 1938) which should be more representative than a simple average. These and other estimates are compared in Table 6 on p. 105.

It must be remembered, however, that according to DALY's (1933) estimate the granites and granodiorites together comprise at least 95% of all intrusive rocks, and basalts and pyroxene andesites about 98% of the extrusives. It is therefore a good approximation for the present purpose to assume that the sediments have been formed not from the average igneous rock but from "granite" and "basalt." These rock types are easier to define than the concept "average igneous rock," and furthermore those rocks that have a chemical composition not conforming to either of the two rock types might, to some extent, be regarded as being composed of these two components, which makes the approximation still better. The frequencies of the two rock types will be determined from the calculations. The revised equation should be:

$$g_x G + b_x B = m_x M + s_x S \qquad (2)$$

where g_x and G refer to granite, and b_x and B to basalt, the notations being analogous to those already used.

THE CHEMICAL COMPOSITION OF "GRANITE" AND "BASALT"

It has been mentioned already that DALY included granodiorite in the granite group in his discussion of the importance of different intrusive rocks. The granodiorites are undoubtedly very important, but it is impossible without an elaborate study to estimate the proportions of "granite proper" and "granodiorite proper" in

Table 1. *Average chemical composition of granite and granodiorite according to* DALY (1933)

	1	2	3	4	
	Granite	*Granodiorite*	*Average of* 1 *and* 2	*Analysis* 3 *recalculated*	
SiO_2	70·77	65·69	68·23	Si	30·38 ± 0·60
TiO_2	0·39	0·57	0·48	Ti	0·29 ± 0·03
Al_2O_3	14·59	16·11	15·35	Al	8·12 ± 0·20
Fe_2O_3	1·58	1·76	1·67		
FeO	1·79	2·68	2·23		
(Fe)	2·50	3·31	2·90	Fe	2·90 ± 0·20
MnO	0·12	0·07	0·10	Mn	0·07
MgO	0·89	1·93	1·41	Mg	0·85 ± 0·20
CaO	2·01	4·47	3·24	Ca	2·32 ± 0·30
Na_2O	3·52	3·74	3·63	Na	2·69 ± 0·05
K_2O	4·15	2·78	3·47	K	2·88 ± 0·10
P_2O_5	0·19	0·20	0·20	P	0·08 ± 0·00
Total	100·00	100·00	—		—

his group. Therefore I have chosen to assume that they are equally frequent, and in order to calculate the average I have used DALY's (1933) well-known averages for "granite" and "granodiorite" (Table 1). This average is probably better than either of the two averages themselves, and the estimated limits of error have been chosen as half of the difference between the average and the analyses.

As is well known there are two different types of basalt, the olivine-basalt magma-type and the tholeiitic magma type. The tholeiitic basalt is associated with continental regions in contrast to the olivine basalt which has a world-wide occurrence. In order to avoid the difficulty of estimating the relative importance of these two types, I have chosen an average of averages from the plateau basalts which might be regarded as the most common type of basalt, and disregarded the influence of pyroxene andesite which is most probably unimportant. For that purpose the compilation made by WALKER and POLDERVAART (1949, p. 649) has been used (Table 2), and it includes most of the important areas. The oceanic islands have not been taken into consideration because the weathering on the ocean bottom must be quantitatively unimportant in comparison to that of land areas, and furthermore the differences in chemical composition of different types of basalts are in the main small in comparison with other rock types. The table is then identical with that presented by BARTH (1952, p. 181). The average is given in column 12 of Table 2 and the limits of error given are the standard deviation of the mean of analyses 1–11.

Table 2. Average chemical composition of various basaltic provinces (after WALKER *and* POLDERVAART (1949))

	1	2	3	4	5	6	7	8	9	10	11	12	*Analysis 12 recalculated*
SiO_2	51·9	52·5	53·3	54·0	51·6	52·2	49·5	51·3	49·8	50·8	50·6	51·55	Si 24·08 ± 0·15
TiO_2	1·1	1·0	0·6	0·7	2·0	1·3	1·5	1·9	1·7	1·5	3·0	1·48	Ti 0·89 ± 0·15
Al_2O_3	15·5	15·4	16·4	16·1	13·5	15·4	14·1	14·0	15·0	15·3	13·9	14·95	Al 7·91 ± 0·15
Fe_2O_3	1·0	1·2	0·5	0·8	5·3	1·6	4·8	3·3	2·7	4·5	2·4	2·55	
FeO	9·7	9·3	8·3	7·4	7·7	8·7	10·1	10·1	10·2	6·9	11·8	9·10	Fe 8·86 ± 0·40
MnO	0·3	0·2	0·2	0·1	0·2	0·1	0·2	0·3	0·2	0·2	0·2	0·20	Mn 0·15
MgO	8·2	7·1	6·7	7·0	6·3	7·3	6·1	5·5	6·5	7·5	4·7	6·63	Mg 4·00 ± 0·20
CaO	9·7	10·3	11·5	11·1	9·8	10·0	9·9	9·8	10·9	8·6	8·3	10·00	Ca 7·15 ± 0·20
Na_2O	1·8	2·1	1·6	1·8	2·4	2·4	2·7	2·8	2·2	3·0	3·0	2·35	Na 1·74 ± 0·10
K_2O	0·7	0·8	0·9	1·0	1·0	0·8	0·7	0·7	0·6	1·3	1·3	0·89	K 0·74 ± 0·05
P_2O_5	0·1	0·1	—	—	0·2	0·2	0·4	0·3	0·2	0·4	0·8	0·30	P 0·13 ± 0·03

1. Average Karroo chilled basalt
2. Average Karroo dolerite
3. Average Tasmania chilled basalt
4. Average Antarctica dolerite
5. Average South America basalt
6. Average Palisade chilled basalt

} Triassic-Liassic

7. Average Spitzbergen basalt
8. Average Deccan basalt

} Cretaceous

9. Average Siberian trap
10. Average Central Victoria lavas. Tertiary
11. Average Oregon basalt. Recent
12. Average of analyses 1–11

THE CHEMICAL COMPOSITION OF SEDIMENTS

Sediments might be studied from at least two different viewpoints, viz. chemical and mechanical. A sharp distinction between these two aspects is not essential in most problems, but in the present case—determining the chemical composition of the typical sediments for a geochemical balance calculation—it is a *sine qua non* to make this distinction. The reason is that by definition the equation derived in a previous paragraph is concerned only with those sediments which by complete

weathering, *i.e.* by a chemical process, have been formed from igneous rocks or from sediments formed by mechanical processes from igneous rocks.

This statement might seem trivial, yet to some extent it is possible to find in all sediments minerals or rock fragments that are only partially weathered or even only mechanically disintegrated igneous rocks. In an actual example it is generally impossible to determine the relative proportions; but it varies from practically nought to a hundred percent. Here it is only necessary to note that for the present discussion an average value from actual sedimentary rocks cannot be used without a critical discussion.

A very brief summary of the genesis of sediments from the geochemical viewpoint is useful for the present discussion and will therefore be given. After complete weathering of an igneous rock only minerals like quartz, corundum, ilmenite, magnetite will be left. Quantitatively all minerals can be neglected in comparison with quartz, and therefore it will be assumed that sandstones in the geochemcial sense consist of pure quartz, *i.e.* 100% SiO_2. It is hardly necessary to mention that actual sandstones rarely satisfy this definition.

Those elements which have gone into solution will be found partly as limestones or dolomites partly as shales consisting mainly of silicates and hydroxides. Some elements remain to some extent in solution and are therefore found in sea water.

From this short review it is obvious that it is much easier to state which sediments are completely devoid of an element than to state how this element is distributed among the other sediments. In Table 3 the presence or absence of common elements in the typical ideal sediments and in sea water have been tabulated. From this table it is seen that some elements are present only in "shales" and in some cases also in sea water. Titanium, aluminium, iron, manganese, phosphorus, sodium and potassium belong to this group.

In Table 4 columns 1–5 the chemical composition of important sediments according to CLARKE (1924) has been tabulated. At least the first three of them

Table 3. Presence or absence of significant amounts of an element in common sediments and sea water

	Sandstone	*Carbonate rocks*	*Shale*	*Sea water*
Si	+	−	+	−
Ti	−	−	+	−
Al	−	−	+	−
Fe	−	−	+	−
Mn	−	−	+	−
Mg	−	+	+	+
Ca	−	+	+	+
Na	−	−	+	+
K	−	−	+	+
P	−	−	+	−

\+ significant constituent
− insignificant constituent

Table 4. The chemical composition of the common sediments (after CLARKE, 1924)

	1	2	3	4	5	6	7
SiO_2	61·16	79·63	5·24	58·61	61·50	61·16	65·08
TiO_2	0·68	0·25	0·06	1·05	1·37	0·68	0·72
Al_2O_3	16·21	4·85	0·82	17·15	18·61	16·21	17·25
Fe_2O_3	4·23	1·09	0·55	9·32	5·46	4·23	4·50
FeO	2·58	0·31	—	0·90	2·48	2·58	2·74
MnO	—	—	—	—	0·12	—	—
MnO_2	—	—	—	1·30	—	—	—
MgO	2·57	1·18	7·96	3·57	2·34	2·11	2·24
CaO	3·27	5·59	42·97	2·11	2·20	0·49	0·52
Na_2O	1·37	0·46	0·05	2·21	1·13	1·37	1·46
K_2O	3·41	1·33	0·33	3·07	2·42	3·41	3·63
CO_2	2·77	5·11	41·93	—	—	—	—
P_2O_5	0·18	0·08	0·04	0·30	0·23	0·18	0·19
Misc.	1·57	0·12	0·05	0·41	2·14	1·57	1·67
Total	100·00	100·00	100·00	100·00	100·00	93·99	100·00
CaO/MgO	1·27	4·75	5·40	0·59	0·94	—	0·23

1. Average shale, waterfree
2. Average sandstone, waterfree
3. Average limestone, waterfree
4. Average of 51 analyses of red deep-sea clay
5. Average of 4 analyses of green mud and 48 analyses of blue mud
6. Analysis 1 corrected for carbonate assuming CaO/MgO = 6 in the carbonate
7. Analysis 6 recalculated to the sum 100·00

represent in no way the pure sediments in the sense used here; on the contrary they are mixtures of the three components "limestone," "shale" and "sandstone." Hence they must be recalculated, but unfortunately this is no straight-forward process.

In the present case it is most important to make a correction for the content of "limestone" in the analysis 1. The CaO/MgO ratio is important for this correction, it varies in the three analyses, but in limestone and sandstone it is around 5. Both of them contain some shale, and therefore we shall assume the correct ratio to be 6. Using this value and the CO_2 value from column 1 we are able to correct this analysis, and to recalculate it to the sum 100·00. This has been done in columns 6 and 7 of Table 4.

The analyses 4, 5 and 7 of Table 4 have been recalculated in the first three columns of Table 5 giving the weight percentages of the elements themselves instead of their oxides. The fourth column of this table gives the values chosen for the present calculations. The main difficulty in their selection is our ignorance of to what extent deep sea sediments contribute to the shales. Their importance has been emphasized especially by KUENEN (1941, 1946, 1950), but he makes no distinction in the sense used here between weathered and unweathered sediments.

The arguments used in order to obtain the values of column 4 are the following. Analysis 1 contains certainly some sandstone, but on the other hand the analyses 2

Table 5. The average chemical composition of various "shales" and sea water

	1	2	3	4	5
Si	30·41	27·38	28·73	28·70 ± 0·50	—
Ti	0·43	0·63	0·82	0·65	—
Al	9·13	9·07	9·85	9·50 ± 0·25	—
Fe	5·28	7·22	5·75	5·75 ± 0·40	—
Mn	—	0·82	0·09	—	—
Mg	1·35	2·15	1·41	1·40 ± 0·20	0·36
Ca	0·37	1·51	1·57	0·40 ± 0·20	0·12
Na	1·08	1·64	0·84	1·00 ± 0·20	3·00
K	3·01	2·55	2·01	2·55 ± 0·10	0·11
P	0·08	0·13	0·10	0·10	—

1. Average shale, waterfree and corrected for carbonate (analysis 7 in Table 4)
2. Average red deep-sea clay (analysis 4 in Table 4)
3. Average green and blue mud (analysis 5 in Table 4)
4. Analysis used as "average shale"
5. Amount of an element in sea water (in kg/cm_e^2)

and 3 are most probably devoid of it. The Si-value of analysis 3 has been chosen because it is almost the average of the other two values and because analysis 2 contains probably too much of oxides-hydroxides. This is also the reason why the limits of error have been chosen as $\pm 0{\cdot}50$.

For titanium the value of analysis 2 has been chosen, because it is almost the average of the three values. This value is admittedly very inaccurate, and no limits of error have been given.

The aluminium value is an average of analyses 1 and 3. The reason for this choice is that probably analysis 1 to some extent includes some undisintegrated feldspar, and this value therefore is too low. The reason for disregarding analysis 2 is the same as for iron. The limits of error are fairly large.

Iron presents a difficult problem because red deep-sea clay constitutes an unknown proportion of the total amount of sediments. The value of analysis 3 has been chosen because its value is larger than the terrestrial shale value of analysis 1, but definitely smaller than the red deep-sea clay value. It is probable that in red deep-sea clay some amounts of undisintegrated pyroxene and olivine occur. The limits of error have been chosen fairly large in this case also.

The same problem is met with when magnesium is studied. For the same reasons as discussed for iron the value of column 3 has been chosen. The estimated inaccuracy is perhaps too small, because it might be expected that the magnesium content of an ideal shale should be quite low.

The calcium values of analyses 2 and 3 are in my opinion too high, and it must be expected that in an ideal shale the calcium content must be very small, because calcium must be primarily fixed mainly by sorption. Therefore the low value of analysis 1 has been chosen, and the limits of error are large in comparison to the chosen value.

The sodium value of red deep-sea clay is definitely too high, and for this reason

it has been disregarded. The sodium value is therefore a rounded-off arithmetic mean between analyses 1 and 3, and the estimated limits of error cover both of these values. Potassium shows a marked variation, and the value of analysis 3 has been chosen as a suitable average of the other two values. The limits of error are in this case probably small.

Phosphorus is given as the average value of the three analyses, and no error has been given on account of the fact that the most important sedimentary phosphate deposits have a genetic relationship to carbonates and it is not easy to take it into account here.

The composition of sea water is given in column 5 of Table 5.

The Calculations

Using the values presented in Tables 1, 2 and 5 the following equations are obtained, where A represents amount of shale

$$\text{Al:} \quad 8{\cdot}12G + 7{\cdot}91B = 9{\cdot}50A \tag{3}$$

$$\text{Fe:} \quad 2{\cdot}90G + 8{\cdot}86B = 5{\cdot}75A \tag{4}$$

$$\text{Na:} \quad 2{\cdot}69G + 1{\cdot}74B = 1{\cdot}00A + 300 \tag{5}$$

$$\text{K:} \quad 2{\cdot}88G + 0{\cdot}74B = 2{\cdot}55A + 11 \tag{6}$$

The equations given by titanium, manganese and phosphorus have not been used because they are less accurately known.

An interesting point in connection with this system of equations is that equations (3) and (4) give a solution in G/B and $A/(G + B)$ and that this solution might be compared with those obtained by solving (5), (6) and the most reliable of the two others, *i.e.* (3). It would be possible to obtain an independent check of the results if good values could be obtained for some other element, *e.g.* titanium.

Solving equations (3) and (4) we obtain

$$G/B = 2{\cdot}02 \pm 0{\cdot}70$$

and

$$A/(G + B) = 0{\cdot}846 \pm 0{\cdot}025$$

The estimates of the limits of error have been obtained by using the common Gaussian error formula for several independent variables:

$$E = \pm \left[\left(\varepsilon_1 \frac{\partial f}{\partial x_1} \right)^2 + \left(\varepsilon_2 \frac{\partial f}{\partial x_2} \right)^2 + \ldots + \left(\varepsilon_n \frac{\partial f}{\partial x_n} \right)^2 \right]^{\frac{1}{2}}$$

where E is the error of $F = f(x_1, x_2, \ldots, x_n)$ and $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n$ are the errors of the n independent variables. It might be argued whether it is permissible to use a formula of this sort in a calculation of the present type, but the limits of errors given here have been calculated simply to give the reader an impression of the order of magnitude of the errors.

An investigation into the sources of the calculated error shows that about 60% of the error in G/B derives from the iron content of shales, the rest mainly from aluminium in shales and iron in basalt and granite. A similar calculation for

$A/(G + B)$ shows that it is mainly the aluminium values which are responsible for the error. The aluminium content of shale represents about 50% and of granite about 30% of the error.

Solving (3), (6) and (7) we get, if cm_e^2 stands for square centimetre of earth's surface

$$G = 134 \pm 16 \text{ kg/cm}_e^2$$

$$B = 60 \pm 14 \text{ kg/cm}_e^2$$

$$A = 164 \pm 27 \text{ kg/cm}_e^2$$

and thus

$$G/B = 2{\cdot}24 \pm 0{\cdot}70$$

and

$$A/(G + B) = 0{\cdot}845 \pm 0{\cdot}022$$

The error of G is mainly dependent on the sodium value of shale (about 60%) and to some extent on the potassium value of the same sediment. The error of B is mainly dependent on the potassium values of shale (about 50%) and granite (about 30%). The error of A is mainly dependent on the sodium value of shale (about 40%) and the potassium values of basalt and granite.

The error of the ratio G/B is mainly dependent on the values of potassium in shale and granite, and the error of the ratio $A/(G + B)$ depends mainly on the accuracy of the values of aluminium in granite and shale.

It is interesting to note that the G/B ratios do not differ more than 0·22, in spite of the fact that their errors are about $\pm 0{\cdot}70$ and that these errors are mainly dependent on different elements. In the first solution it is the iron values and in the second the potassium, in both cases the shale values being most important.

The errors of $A/(G + B)$ are small in both solutions, but the good agreement between the values is not so significant in this case because the aluminium values of shale and granite are in both cases mainly responsible for the errors.

The following averages will be used in the calculations of the next paragraph

$$G/B = 2{\cdot}13 \pm 0{\cdot}70$$

$$A/(G + B) = 0{\cdot}845 \pm 0{\cdot}022$$

The Chemical Composition of the Average Igneous Rock

It is now possible to calculate the chemical composition of the average igneous rock which has weathered into the sediments. We have only to use the ratio G/B calculated above, the analysis 3 of Table 1 and analysis 12 of Table 2. In columns 1–3 of Table 6 the results are shown and in the other columns of this table other estimates are presented for a comparison with them. The column 2 is calculated with $G/B = 2{\cdot}13$ and 1 and 3 with $2{\cdot}13 - 0{\cdot}70 = 1{\cdot}43$, and $2{\cdot}13 + 0{\cdot}70 = 2{\cdot}83$, *i.e.* using the estimated limits of error.

If we compare these first three columns with each other it is evident that the possible variations in the chemical composition of the average igneous rock are not very large.

If we compare column 2 with the other estimates a remarkable similarity, or

Table 6. The composition of the "average igneous rock" calculated from the ratio granite/basalt, and other estimates of their composition

	1	2	3	4	5	6	7	8	9	10
SiO_2	61·45	62·90	63·90	59·86	68·31	63·83	62·43	64·03	65·73	59·19
TiO_2	0·89	0·80	0·74	1·06	0·42	0·82	0·74	0·60	0·55	0·79
Al_2O_3	15·19	15·22	15·24	15·53	14·82	16·95	15·91	15·71	15·41	15·82
Fe_2O_3	2·02	1·96	1·90	3·12	1·29	2·41	2·95	2·20	2·10	3·41
FeO	5·05	4·43	4·02	3·85	3·17	2·94	3·29	2·66	2·30	3·58
Fe_{total}	5·34	4·81	4·45	5·17	3·36	3·98	4·62	3·61	3·16	5·17
MnO	0·14	0·13	0·13	0·12	0·04	0·02	0·16	—	—	0·11
MgO	3·55	3·08	2·76	3·53	1·71	1·80	3·01	2·67	2·23	3·30
CaO	6·01	5·40	5·00	5·14	3·43	4·12	5·12	4·62	4·01	3·07
Na_2O	3·10	3·22	3·30	3·89	3·10	3·68	3·44	3·51	3·43	2·05
K_2O	2·42	2·65	2·80	3·17	3·60	3·11	2·68	3·52	3·79	3·93
P_2O_5	0·24	0·23	0·23	0·30	0·11	0·22	0·26	0·18	0·17	0·22
FeO/Fe_2O_3	2·50	2·26	2·12	1·23	2·46	1·22	1·11	1·21	1·10	1·05

1. Igneous rocks from $G/B = 1·43$
2. Igneous rocks from $G/B = 2·13$
3. Igneous rocks from $G/B = 2·83$
4. Igneous rocks (Clarke and Washington, 1924)
5. Pre-Cambrian rocks of Finland (Sederholm, 1924)
6. Canadian Shield (Grout, 1938)
7. Cordilleran and Appalachian rocks (Knopf, 1916)
8. Igneous rocks, hypothesis I (J. H. L. Vogt, 1931)
9. Igneous rocks, hypothesis II (J. H. L. Vogt, 1931)
10. Norwegian glacial clay (V. M. Goldschmidt, 1933)

almost identity, is observed between columns 2 and 7, *i.e.* between the present calculation and the values found by A. Knopf (1916) for the Cordilleran and Appalachian rocks. He determined the areas occupied by all the different igneous rocks on the geological maps of the above-mentioned regions, and calculated their average chemical composition using Daly's type values.

There is one exception to this remarkable similarity between the two analyses, however, namely the ratio FeO/Fe_2O_3, which in the present calculation comes out too high in comparison with the American rocks. The total iron on the other hand corresponds very closely in the two analyses. The fact that the observed rocks show a higher degree of oxidation is symptomatic, and it is probably related to the oxidation processes going on in the neighbourhood of the earth's surface; but it is most difficult to make a complete interpretation of it at present.

One interesting point is that those areas which have been deeply denudated like Finland (column 5) and the Canadian Shield (column 4), do not show the same degree of similarity to analysis 2 as analysis 7. In my opinion this is not casual but an important fact. The reason for this belief is that we have not calculated the "average igneous rock in general" but the average igneous rock which has given rise to the sediments. Erosion and weathering is enormously more active in a mountainous region than in a peneplaned low-land. Consequently an area

like the Rocky Mountains must show a much closer relationship to the rocks which formed the sediments than those occurring in Finland and similar regions.

Checking the literature I found that the present method is almost identical with one used by W. J. Mead as early as 1914, and which had been partly anticipated by F. Loewinson-Lessing (1911) by emphasizing the dominating importance of basalt and granite. Mead using the data available at that time obtained for the ratio G/B the value 1·86; *i.e.* well within the limits of error equal to the present result.

The main difference is that Mead did not consider the influence of sea water and its dissolved salts on his results. Therefore it was impossible for him to get the absolute values, but in principle the present calculations are only a modernized version of Mead's ideas.

The Total Amount of Sediments

We have already found that

$$G = 143 \pm 16 \text{ kg/cm}_e^2$$

$$B = 60 \pm 14 \text{ kg/cm}_e^2$$

$$A = 164 \pm 27 \text{ kg/cm}_e^2$$

These values might be used to calculate the total amount of sandstone from the Si-values.

$$30{\cdot}38 \times 134 + 24{\cdot}08 \times 60 = 28{\cdot}70 \times 164 + 46{\cdot}72 \times Q \qquad (7)$$

$$Q = 17{\cdot}3 \pm 21 \text{ kg/cm}_e^2$$

The error is in this case mainly dependent on the inaccuracies of the G, B and A (about 60%) values, and it is evident that the value found only gives the order of magnitude.

From the calcium and magnesium values the amount of carbonate rocks might be calculated.

$$\text{Ca:} \quad 2{\cdot}32 \times 134 + 7{\cdot}15 \times 60 = 0{\cdot}40 \times 164 + 0{\cdot}12 \times 100 + 100x \qquad (8)$$

$$\text{Mg:} \quad 0{\cdot}85 \times 143 + 4{\cdot}00 \times 60 = 1{\cdot}40 \times 164 + 0{\cdot}36 \times 100 + 100y \qquad (9)$$

Magnesium carbonate contains 28·84% Mg and calcium carbonate contains 40·04% Ca. Thus equations (8) and (9) might be rewritten

$$\text{Ca:} \quad 2{\cdot}32 \times 134 + 7{\cdot}15 \times 60 = 0{\cdot}40 \times 164 + 0{\cdot}12 \times 100 + 40{\cdot}04C \qquad (10)$$

$$\text{Mg:} \quad 0{\cdot}85 \times 134 + 4{\cdot}00 \times 60 = 1{\cdot}40 \times 164 + 0{\cdot}36 \times 100 + 28{\cdot}84M \qquad (11)$$

The solutions are

$$C = 16{\cdot}5 \pm 3{\cdot}1 \text{ kg/cm}_e^2$$

$$M = 3{\cdot}1 \pm 2{\cdot}9 \text{ kg/cm}_e^2$$

The error of the calcium carbonate value is mainly dependent on the error of B (about 2/3 of it) and to a lesser degree on the error of the G value and the calcium

values of granite and shale. The error of the magnesium carbonate value is mainly dependent on the error of B (about 50% of the estimated error) and to a lesser extent on A, and the magnesium values of granite and shale. Summarizing these results we have found the following values: shale 164 ± 27 kg/cm$_e^2$, sandstone $17{\cdot}3 \pm 21$ kg/cm$_e^2$, calcium carbonate $16{\cdot}5 \pm 3{\cdot}1$ kg/cm$_e^2$ and magnesium carbonate $3{\cdot}1 \pm 2{\cdot}9$ kg/cm$_e^2$. However, it must be remembered that the shale has been calculated waterfree, and therefore the result must be corrected before a comparison can be made with previous results. Assuming 5% water in the shales the corrected value will be 172 ± 28 kg/cm$_e^2$. The total amount of sediments will be $208{\cdot}9 \pm 35$ kg/cm$_e^2$ after this correction, or almost exactly

$$209 \pm 35 \text{ kg/cm}_e^2$$

This value is equivalent to a total mass of the sediments of

$$(4{\cdot}1 \pm 0{\cdot}6) \times 10^8 \text{ km}^3$$

Clarke (1924) and Goldschmidt (1933) both found an almost identical result $3{\cdot}7 \times 10^8$ km^3, Borchert (1951) $4{\cdot}4 \times 10^8$ km^3. Kuenen has criticized all values of this magnitude in several papers (1941, 1946), and he has been able to show that the total amount of sediments must be much larger than the values obtained in these and similar papers. However, he made no difference between sediments formed from fresh and weathered igneous rocks. As already mentioned this point is essential, because a calculation based on chemical changes is not able to take account of a mechanical transport.

Two of his arguments are of special interest here (Kuenen, 1946, p. 570), *viz.* the geochemistry of titanium and that of phosphorus. He stresses the fact that it is impossible to obtain a proper balance for these elements if not large amounts of deep-sea sediments are included in the balance. It is of some interest therefore to see how the present figures work out. For titanium the equation will be

$$134 \times 0{\cdot}29 + 60 \times 0{\cdot}89 = 164x$$

$$x = 0{\cdot}56 \pm 0{\cdot}14\% \text{ Ti}$$

Quite dominating in the square sum of this error are the terms from A and B. The value obtained is definitely larger than that of ordinary terrestrial shale, and it is also definitely smaller than the value given for green and blue mud in Table 5. On the whole it must be said that the value obtained is quite probable, that it agrees with the estimate of Table 5 within the limits of error and that the balance is satisfied.

For phosphorus we have

$$134 \times 0{\cdot}08 + 60 \times 0{\cdot}13 = 164y$$

$$y = 0{\cdot}113 \pm 0{\cdot}024\% \text{P}$$

The situation is here the same as in the case of titanium, the error is mainly dependent of the inaccuracies of A and B. The present value is also consistent with the values given in Table 5, and therefore the argument of Kuenen is not valid for the present calculation.

In order to discuss the detailed distribution the results of previous calculations are compared with the present one in Table 7.

Table 7. A comparison between the results of different investigators concerning the total amount of sediments and their distribution

	Weathered igneous rocks in kg/cm$_2^2$	$\frac{A}{E}$ or $\frac{A}{G+B}$	$\frac{A+Q}{E}$ or $\frac{A+Q}{G+B}$	*Shale (kg/cm$_2^2$)*	*Sandstone (kg/cm$_2^2$)*	*Shale + sandstone (kg/cm$_2^2$)*	*Calcium carbonate (kg/cm$_2^2$)*	*Magnesium carbonate (kg/cm$_2^2$)*	*Dolomite (kg/cm$_2^2$)*	*"Limestone" (kg/cm$_2^2$)*	*Carbonate rocks (total) (kg/cm$_2^2$)*	*Total amount of sediments (kg/cm$_2^2$)*
V. M. GOLDSCHMIDT (1933)	160	—	0·97	—	—	155	12·6	2·0	4·4	10·2	14·6	170
W. v. ENGELHARDT (1936)	160	0·844	0·97	135	20	155	12·6	2·0	4·4	10·2	14·6	170
K. KALLE (1943)	157	0·846	0·97	132·9	19·1	152	12·3	1·9	4·2	10·0	14·2	166
H. BORCHERT (1951)	190	0·97	1·11	184	27	211	16·5	2·5	5·4	13·6	19·0	230
This paper	194 ± 21	0·845[1] ± 0·022	0·93	172 ± 28	17·3 ± 21[2]	189 ± 35	16·5 ± 3·1	3·1 ± 2·9	6·8 ± 3·0	12·8 ± 4·3	19·6 ± 4·2	209 ± 35

[1] Waterfree, with 5% H_2O 0·89

[2] From normative quartz 32·8

The sandstone value is obviously not very accurate, giving only the order of magnitude. A comparison with the values of ENGELHARDT (1936), KALLE (1943) and BORCHERT (1951) shows that it is of the same order. If sandstone is included in shale, the value obtained is not far from the average of the values of GOLDSCHMIDT and BORCHERT, and they are both included within the present limits of error.

Dr. J. EKLUND has pointed out to me that sandstone (quartz) will derive almost exclusively from granite. If the norm of the "granite" analysis is calculated the normative quartz is found to be 24·5%, *i.e.* equivalent to 32·8 kg sandstone. This value will be an upper limit.

The carbonate rocks are definitely more common according to the present results than according to GOLDSCHMIDT'S, but they are very similar to the results published by BORCHERT.

The magnesium carbonate value gives only the magnitude, and therefore the dolomite value is also very uncertain. The ratio sandstone to carbonate rocks is somewhat smaller than 1 according to the present results, which is contrary to the results of all previous investigations.

The shale value has been calculated on the assumption of a water content of 5 per cent. This assumption is arbitrary, but the correct value must be somewhere between 2 and 8 per cent. An error in this value is not important, however, because the inaccuracy of the waterfree shale value is comparatively large.

SOME GENERAL REMARKS

It is quite evident that the calculations presented in the previous paragraphs could be improved if we had a better knowledge of the distribution of the chemical elements. If it were known for a larger number of elements, there would be more equations than unknowns.

This problem is mathematically interesting, because it is of a type which has been much studied during recent years in econometrics (REIERSØL 1950, NEYMAN 1951) as has been kindly pointed out to me by Prof. H. CRAMÉR. We have equations

$$a_\nu x + b_\nu y + c_\nu z = d_\nu$$

where the most plausible values of x, y and z shall be determined and where a_ν, b_ν, c_ν and d_ν have errors which are mainly independent of each other. Curiously enough this problem has sometimes no solution, depending on the distributions of the errors of the coefficients!

These problems have no actual interest to geochemistry, until we are able to write down at least a dozen or more equations with some confidence.

At that time it will also be possible to control the hypothesis that the original ocean water was devoid of cations like sodium and potassium. In the previous paragraphs all results have been calculated without taking into account the errors deriving from the inaccuracies in the values of sodium and potassium in sea water. It must be remembered, however, that there are two factors working in opposite directions and the net effect of them is therefore very difficult to estimate. On one hand the sea-water values must be diminished by the original contents of the chemical elements in sea water, and on the other they must be increased with the

amounts represented by the evaporites and salt solutions in the pore space of sediments. Even if the net effect is not negligible, an investigation shows that fortunately many of the calculated values are insensitive to errors in these values.

The present calculations are only concerned with the net balance of the elements and they do not take time-dependent properties of sediments into account. It has been found, for instance, that progressively younger shales contain successively less Al_2O_3, FeO, total iron, K_2O and C, and successively more CaO, P_2O_5, moisture, CO_2 and SO_3 (cf. Nanz, 1953). These discoveries have only importance in this connection by influencing the selection of the typical analysis.

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Statistical methods applied to geochemistry

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ABSTRACT

Geochemistry is a fruitful field for the application of statistical methods, which provide the best techniques for handling the large quantities of data appearing in the literature. The three basic geochemical procedures—sampling, analyzing and comparing results—are governed by statistical theory. Each is reviewed in the text.

Analysis by spectrographic methods is best considered as a problem in linear regression theory; the necessary procedure and results are described in terms of the analysis of shales for gallium.

Results are best compared by the use of discrimination tests and confidence intervals. Several examples are given to illustrate the methods. It is shown how this procedure establishes clear and valid differences in composition, which appear small and perhaps insignificant at first sight.

Introduction

At the present time geochemistry is passing into its third phase of development as a science. The first stage roughly comprised the nineteenth century, when methods of gravimetric analysis improved until the composition of most minerals could be determined (Berzelius, Bischof, Roth). At the end of the century the second stage was developing concurrently as the average composition of the crust of the earth began to be studied. This culminated in the discovery of the laws governing the distribution of elements in terrestrial and cosmic materials, the establishment of the orders of magnitude of abundance of most elements and the completion of a general outline of the chemical history of the earth. Among the many men connected with this stage, three stand out above all, Clarke, Vernadsky and Goldschmidt. The third phase is developing as new geochemical studies are made, and is at present characterized by the abundance and precision of the data. Much of the earlier work on element abundances needs revision and more quantitative expression, which would be impossible but for the great improvements in analytical techniques during the last fifteen years.

In the past it has proved unwise to compare minor element analyses made by different laboratories, especially when the spectrograph has been used. Indeed there is evidence that it is even now unwise to compare gravimetric results in the same manner (e.g., Fairbairn *et al.*, 1951, p. 7). This was due to inadequate knowledge of the analytical errors in the methods used, and was a highly undesirable state of affairs.

There is only one way in which this situation can be improved, and that is to realize that the three basic geochemical procedures—*sampling*, *analyzing* and *comparing results* are governed fundamentally by statistical theory and to act in accordance with this fact. The present paper is therefore written to demonstrate some statistical methods which have proved valuable in practice. Much of what follows will be elementary to those familiar with statistics, but may be of use to those who graduated from the ranks of geologists, leaving mathematics far behind.

Numerous reference books are available and particular mention is made of Davies (1949), Mood (1950), and Dixon and Massey (1951). As a general introduction to the theory of statistics for the non-mathematical reader Moroney (1951) will be of value.

In the following the three basic procedures mentioned above will be considered separately.

Sampling

On the whole, the difficulties of sampling rocks are well known and have been discussed on numerous occasions; e.g., Grout (1932) has treated the subject from the geochemists' point of view. It must be clearly understood whether the sample is to represent a hand-specimen, an outcrop or a formation, and the procedure will vary accordingly. If it is required to find the average of a certain rock type, e.g., diabase, then the best procedure is to sample and analyze separately a large number of diabase intrusions. The reprehensible practice of making composite samples has only one merit, that it saves labour. For diabase has no fixed composition, and from a large number of analyses the range of variation can be established to any required degree of probability. In fact the range is as useful as the average value, or in statistical terms the standard deviation is as valuable as the mean. For example, Fairbairn, Ahrens and Gorfinkle (1953) analyzed 28 Ontario diabases (excluding Nipigon-type rocks) for numerous elements, including rubidium. The average Rb content (m) was 144 ppm, with a standard deviation (s) of 86. Statistical theory then states that if another diabase were analyzed there is a probability of about 0·68 that its Rb content will lie between $m \pm s$, i.e., between 58 and 230 ppm, and about 0·95 probability that it will lie in the range $m \pm 2s$, i.e., between 0 and 316 ppm. In other words, one analysis in twenty might lie outside this latter range. If, instead of analyzing 28 separate rocks, they had analyzed a composite sample, its Rb content would probably have been close to the mean of 144 ppm but there would have been no information on the range in composition, which is essential if it is desired to test whether some subsequent diabase is of the same composition.

In most geochemical work there is one good rule for sampling: the more samples, the better.

Analyzing

If results are to be compared it is essential to know the precision and accuracy of the analytical method. The two are not the same. Precision refers to the ability to duplicate results; accuracy refers to the closeness between the results and the "true value," which is of course unknowable. Measurements of accuracy are difficult to make and are best treated by comparisons of analyses of *standard samples*, which have been analyzed by several methods in numerous laboratories. This is done extensively in the metallurgical industries and has started in geochemistry with the analytical study of a standard diabase and granite made by Fairbairn *et al* (1951). With careful consideration of analytical methods the problem of accuracy is probably not so difficult as many believe.

Measurements of precision are easy to obtain, but are seldom seen in the literature. For gravimetric methods this is understandable, since repeats are laborious.

For the spectrograph there is no excuse, since repeats can be obtained quickly and cheaply and precision measurements are important for this instrument.

The customary procedure with the spectrograph is to set up a working-curve by measuring the blackness of photographed spectral lines for a series of standard mixtures, whose composition is known. There are numerous methods and detailed procedures are available in AHRENS (1950) and MITCHELL (1948). Usually the working-curve is linear over most of its length (Fig. 1) and easy to fit. To be fully consistent in the statistical approach the working-curve should be fitted by a linear regression analysis, commonly referred to as "the least-squares method." There are several least-squares methods and it is important to choose the correct one. As a result one has a working-curve which is the best fit for the data and moreover a contribution to the precision determination is also available. An analogous problem is treated by MOOD (1950, p. 300) and is adapted as follows.

Let a certain standard mixture contain k_i ppm gallium and let $\log k_i = x_i$. Gallium is the analysis element and indium is to be used as internal standard. By measurement of the blackness of the photographed spectral lines of the two elements and their background, it is possible to find the ratio of the emitted light intensities (I_{Ga} and I_{In}). If $y = \log \frac{I_{Ga}}{I_{In}}$, then it is usual to find a linear relation between x and y, which can be expressed as

$$y = \alpha + \beta x$$

A number of standards are exposed (n) and a series of y-values (y_i) are obtained. These are to be fitted to a straight line with the corresponding values x_i. Using a circumflex to indicate the best estimate of any quantity, it is found that

$$\hat{\beta} = \frac{\sum_{i=1}^{n} (y_i - \bar{y})(x_i - \bar{x})}{\sum_{i=1}^{n} (x_i - \bar{x})^2}$$

$$\hat{\alpha} = \bar{y} - \hat{\beta}\bar{x}$$

where $\bar{y}$ and $\bar{x}$ are the average values for y and x. As an example, the values of x and y given in Table 1 are plotted on Fig. 1. The calculations are made simpler by writing

$$\hat{\beta} = \frac{A}{B}$$

where

$$A = \sum_{i=1}^{n} x_i y_i - \frac{\left(\sum_{i=1}^{n} x_i\right)\left(\sum_{i=1}^{n} y_i\right)}{n}$$

and

$$B = \sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} x_i\right)^2}{n}$$

Table 1. *Standard data for gallium*

x*	y
0·5	− 0·40
0·5	− 0·42
1·0	− 0·06
1·0	− 0·06
1·5	+ 0·33
1·5	+ 0·35
1·11	+ 0·17
1·11	+ 0·01
1·11	+ 0·01
1·11	+ 0·02
1·26	+ 0·19
1·26	+ 0·12
1·26	+ 0·33
1·26	+ 0·13
1·26	+ 0·13
1·60	+ 0·44
1·60	+ 0·21
1·60	+ 0·37
1·60	+ 0·46
1·60	+ 0·39
1·60	+ 0·35
1·60	+ 0·35
2·03	+ 0·92
2·03	+ 0·78
2·03	+ 0·81
2·03	+ 0·79
2·03	+ 0·90
2·03	+ 0·73
2·03	+ 0·73

* $x = \log_{10} k$; i.e. when $k = 10$ ppm then $x = 1$, and when $k = 316$ ppm then $x = 2{\cdot}5$.

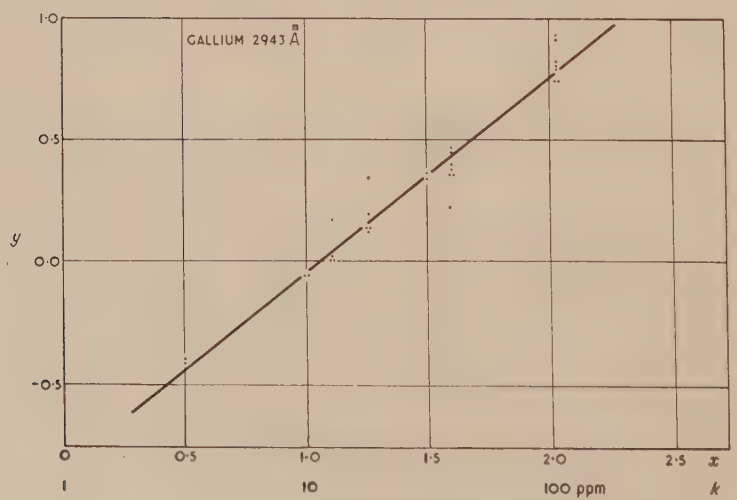

Fig. 1. Working curve for gallium.

On working out the calculations $A = 4{\cdot}2616$

$B = 5{\cdot}3699$

whence $\hat{\beta} = +0{\cdot}794$

and $\hat{\alpha} = -0{\cdot}841$

The regression equation is therefore

$$y = -0{\cdot}841 + 0{\cdot}794x \qquad (1)$$

and is plotted in Fig. 1. The reason for using a regression line of the form $y = \alpha + \beta x$ is given by DAVIES (1949, pp. 125–133) and by EISENHART (1939).

To analyze an unknown the values of y'_j are measured for m replicates, the mean $\bar{y}'$ is calculated and equation (1) is used to find the value

$$x_0 = (\bar{y}' - \hat{\alpha})/\hat{\beta}$$

In general m will be small, and most samples are probably analyzed in triplicate.

Two sets of data can be used to measure the precision. First the spread of the standard points around the line representing equation (1) yields an estimate of the standard deviation of y (s_1), where

$$s_1^2 = \frac{C}{n-2} = \frac{\sum_{i=1}^{n} (y_i - \hat{\alpha} - \hat{\beta}x_i)^2}{n-2}$$

Second, the standard deviation of y' for the unknown is s_2, where

$$s_2^2 = \frac{D}{m-1} = \frac{\sum_{j=i}^{m} (y_j' - \bar{y}')^2}{m-1}$$

The final estimate of the standard deviation of y is s_y, where

$$s_y^2 = \frac{C+D}{n+m-3}$$

and the standard deviation of x_0 is s_{x_0}, where

$$s_{x_0}^2 = \frac{s_y^2}{\hat{\beta}^2}\left[\frac{1}{m} + \frac{1}{n} + \frac{(\bar{y}' - \bar{y})^2}{B\hat{\beta}^2}\right]$$

where B was defined on page 113 and s_{x_0} is in logarithmic units (DAVIES, p. 154).

Returning to the gallium example, the calculations are simplified by expressing the quantity C as follows

$$C = \sum_{i=1}^{n} y_i^2 - \frac{\left(\sum_{i=1}^{n} y_i\right)^2}{n} - \hat{\beta}^2 B$$

and from the data in Table 1 it is found that

$$C = 0{\cdot}1634$$

One sample was analyzed m times ($m = 9$), giving the data in Table 2, from which it is found that

$$D = \sum_{j=1}^{m} y'^2_j - \frac{\left(\sum_{j=1}^{m} y'_j\right)^2}{m} = 0{\cdot}0689$$

Table 2. Replicate analyses on an unknown

j	y'
1	0·49
2	0·36
3	0·32
4	0·30
5	0·25
6	0·49
7	0·29
8	0·31
9	0·24

Hence

$$s_y^2 = \frac{C + D}{n + m - 3} = 0{\cdot}006638$$

and

$$s_{x_0}^2 = 0{\cdot}001535$$

whence

$$s_{x_0} = 0{\cdot}0392$$

Also it is found that $x_0 = 1{\cdot}486 = \log k_0$ whence $k_0 = 31$ ppm. The standard deviation s_{x_0} can be used to express the probability that the value of x_0 is close to the true value m_0. This probability is expressed in terms of a confidence interval as will be explained later.

The value of this procedure is that it gives a clear statement of what sort of consistency can be expected in the results of analysis—far better than the common and misleading expression "the results are correct to within $\pm 10\%$" which is meaningless. If analytical results are to be compared with each other it is essential to know how much of the variation in a suite of analyses is due to analytical error and how much is a real range in composition.

Comparing Results

Discrimination tests

It is unwise to compare a single analysis of one specimen with a single analysis of another, unless they are very different indeed and unless there are grounds for believing that the precision is high. The errors inherent in the sampling and analytical procedures may give a completely wrong impression of the similarities and differences between the specimens. Nevertheless these comparisons are very common, especially with gravimetric analyses. Of course, the instinct of an experienced man will do a great deal to avoid the pitfalls, especially if he is an analyst himself. But most petrologists are not analysts, and the illuminating results of Fairbairn *et al* (1951) show that the precision of rock analysis is not always high. Moreover even the experienced man may err on the side of caution when there is only a small difference in composition, which may none the less be valid; however, the opposite state of affairs is perhaps more common.

It seems likely that the field of analysis where the application of statistics may be the most fruitful is spectrochemistry, where precision may be low but replicate analyses can be carried out cheaply and quickly. Accordingly this section will be concerned chiefly with spectrographic results, some of which are being published elsewhere.

The comparison of sample averages may be made by either the u-test or the t-test, which are described below. For the u-test it is assumed that one sample has been drawn from a normal distribution with mean m_1 and standard deviation σ, indicated by the notation $N(m_1, \sigma^2)$, while the other sample comes from a $N(m_2, \sigma^2)$. We wish to test the *null-hypothesis* that the population means are the same, i.e.,

$m_1 = m_2$. Let $\bar{x}_1$ and $\bar{x}_2$ be the means of the first and second sample, respectively. Then $\bar{x}_1 - \bar{x}_2$ is normally distributed according to

$$N\left(m_1 - m_2, \sigma^2\left(\frac{1}{n_1} + \frac{1}{n_2}\right)\right)$$

where n_1 and n_2 denote the number of observations in the first and second sample. Let

$$u = (\bar{x}_1 - \bar{x}_2)/s_d$$

where

$$s_d = s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}} \text{ and } s^2 = \left[\sum_{i=1}^{n_1}(x_i - \bar{x}_1)^2 + \sum_{j=1}^{n_2}(x_j - \bar{x}_2)^2\right]/(n_1 + n_2 - 2).$$

The expression $\sum_{i=1}^{n_1}(x_i - \bar{x}_1)^2$ is the sum of squares of the deviations of the observations in the first sample from their mean. If $m_1 = m_2$, u is approximately normally distributed with zero mean and unit standard deviation.

From Table 4 (Dixon and Massey, 1951) obtain the value $u_{0\cdot975} = 1\cdot96$ (given as z) such that the probability that u will exceed this value by chance is 0·025. Hence, if $m_1 = m_2$, u should fall outside the interval from $-1\cdot96$ to 1·96 only about 5% of the time. If the calculated value of u falls outside this range, the hypothesis $m_1 = m_2$ is rejected and the decision is reached that the samples come from populations with different means. The test is said to be carried out at the 5% *significance level* which means that the test will lead to incorrect conclusions about 5% of the time. If the experimenter prefers, he can carry out the test at a 1% level or at an even lower level but it is clear that, if this process is carried too far, he will always accept the null-hypothesis and never draw any significant conclusions at all. The significance level must be set by the experimenter.

A complete example will now be worked out. The lead content of 13 low-grade shales averages 16·1 ppm, whereas the average for 30 high-grade schists derived from the others by metamorphism is 27·3 ppm. The respective values for the sums of squares for computing s^2 are 1128·4 and 3462·0. Then

$$s^2 = (1128\cdot4 + 3462\cdot0)/41 = 111\cdot961,$$

whence $s = 10\cdot58$, and $s_d = 3\cdot51$. The value of u is 3·19 which exceeds both $u_{0\cdot975} = 1\cdot96$ and $u_{0\cdot995} = 2\cdot58$ so that it is seen that there is a real difference in the lead content of low and high-grade rocks at the 1% level even though the difference in the sample means is only a few ppm.

The u-test is subject to a certain criticism. The distribution of u is not normal but is what is known as the *Student t-distribution*. This is also a symmetrical distribution whose limiting form, as the sample size increases without limit, is the normal distribution. Critical values are tabulated for the t-distribution just as they are for the normal distribution. The form of the t-distribution, and hence the critical values, depend upon a parameter which statisticians call the *number of degrees of freedom*. In the problem being considered, this parameter is $n_1 + n_2 - 2 = 41$. Rename u as t and enter Table 5 (Dixon and Massey, 1951) with 41 degrees of freedom to find $t_{0\cdot975} = 2\cdot02$ and $t_{0\cdot995} = 2\cdot70$, approximately. It will be noted that

these values are larger than the corresponding critical values for u. Thus, while the same conclusion is reached at the 1% level in this case (since $t = 3{\cdot}19$ is greater than $t_{0{\cdot}995} = 2{\cdot}70$) such would not have been the case if the calculated t had fallen between $t_{0{\cdot}995} = 2{\cdot}70$ and $u_{0{\cdot}995} = 2{\cdot}58$. The difference between these critical values is not large since the number of degrees of freedom, 41, is relatively great, but the difference increases as the number of degrees of freedom decreases. For example, if $n_1 + n_2 - 2 = 9$, then $t_{0{\cdot}995} = 3{\cdot}25$. Thus, in borderline cases, the u-test may lead to the conclusion that a result is significant when it is actually due to chance variations.

It has been assumed also that both samples come from populations with a common standard deviation. This assumption should be verified by making use of the F-test where F is defined by the equation

$$F = s_1^2/s_2^2$$

where

$$s_1^2 = \sum_{i=1}^{n_1} (x_i - \bar{x}_1)^2/(n_1 - 1) \text{ and } s_2^2 = \sum_{j=1}^{n_2} (x_j - \bar{x}_2)^2/(n_2 - 1).$$

The statistic F has a distribution which depends on two parameters $n_1 - 1$ and $n_2 - 1$ known as its degrees of freedom. In setting up F the larger s^2 is put in the numerator, that is, it is assumed that the notation is such that s_1^2 is greater than s_2^2. In the example considered earlier

$$s_1^2 = 94{\cdot}0, \quad s_2^2 = 119{\cdot}4$$

and, putting the larger value in the numerator, $F = 1{\cdot}27$. Entering Table 7 (Dixon and Massey, 1951), it is found that $F_{0{\cdot}975} = 2{\cdot}96$ and $F_{0{\cdot}995} = 4{\cdot}33$, approximately. If the two populations have equal standard deviations, F will exceed $F_{0{\cdot}975}$ ($F_{0{\cdot}995}$) 5% (1%) of the time. If the calculated value of F exceeds the critical value, the hypothesis of equal standard deviations is rejected at the corresponding level of significance. Care should be taken in looking up the critical values of F since a common error is to use $F_{0{\cdot}95}$ which leads to a 10% level of significance.

It has been assumed that the samples come from normal distributions. This assumption is commonly made although it requires a large number of observations to verify it. Figs. 2 and 3 show histograms for the distribution of nickel and zirconium in 63 schists (Shaw, in press) and it can be seen that although for nickel there is a strong tendency towards a unimodal symmetric curve the distribution of zirconium is quite asymmetric. Two similar histograms, for gallium and zirconium oxides in diabase specimens, are given by Ahrens and Gorfinkle (1950) together with fitted normal curves. The t-test requires that the observations come from normal distributions while it is sufficient for the u-test if the means $\bar{x}_1$ and $\bar{x}_2$ are normally distributed. A result that is often quoted in support of the use of the u-test is a theorem which states that, for almost any population, the averages of samples of size n are closer to normality than the original observations and the larger n the better the approximation. However, nothing seems to be known as to how large n should be for this to be a good approximation. In spite of this argument, it is recommended that the t-test always be used since it is a more conservative

test than the u-test. The F-test also involves normality assumptions but there is evidence, presented by COCHRAN (1947), that moderate departures from normality only affect the significance levels by a few percent. If the experimenter is doubtful about the normality of his data, a lower level of significance can be used or more observations made.

It remains to consider what should be done when the F-test indicates that the samples come from populations with different standard deviations. In this case

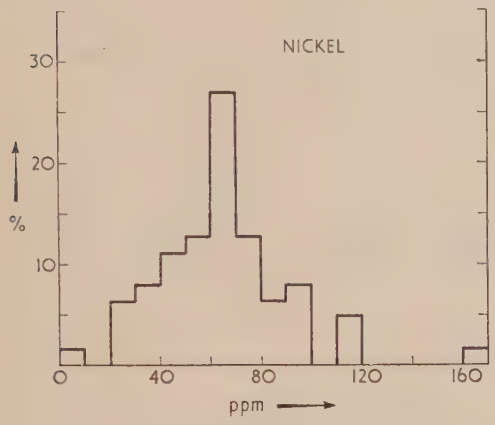

Fig. 2. Distribution of nickel in 63 shales and schists.

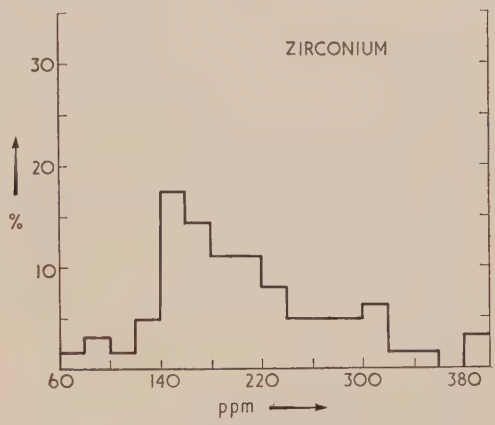

Fig. 3. Distribution of zirconium in 63 shales and schists.

modifications of the u-test and the t-test will be considered. They will be illustrated by the following example. The lithium content of the 13 low-grade shales considered earlier had an average of 54·7 ppm and for the 30 high-grade schists the average was 127·2 ppm. Using the notation given earlier, $s_1^2 = 524$ and $s_2^2 = 4640{\cdot}8$ while $F = 8{\cdot}86$. The critical value for F at the 1% level is 4·33. Since F exceeds this value, the assumption of equal standard deviations must be rejected.

To apply the modified u-test, compute the expressions

$$w_1 = s_1^2/n_1 = 524/13 = 40{\cdot}31, \quad w_2 = s_2^2/n_2$$
$$= 4640{\cdot}8/30 = 154{\cdot}69, \quad s_d = \sqrt{w_1+w_2} = 13{\cdot}96$$

Then

$$u = (\bar{x}_2 - \bar{x}_1)/s_d = (127{\cdot}2 - 54{\cdot}7)/13{\cdot}96 = 5{\cdot}19$$

Recalling that $u_{0{\cdot}995} = 2{\cdot}58$, it is seen that this result is significant at the 1% level.

The modified t-test, as described by COCHRAN and COX (1950, pp. 91–92), differs from the modified u-test only in the critical value that is used. Denote by t_1 and t_2 the critical values of t for $n_1 - 1$ and $n_2 - 1$ degrees of freedom, respectively, for the chosen significance level. At the 5% level, $t_1 = 2{\cdot}18$ and $t_2 = 2{\cdot}05$. Then compute

$$t' = (w_1t_1 + w_2t_2)/(w_1 + w_2) = 2{\cdot}08.$$

The value t' is the appropriate critical value for a 5% test, and is exceeded by $t = 5{\cdot}19$. Actually the computation of t' was not necessary in this case since t'

always lies between t_1 and t_2 which are both less than 5·19. At the 1% level $t_1 = 3{\cdot}05$ and $t_2 = 2{\cdot}76$ so that the difference is significant at this level also.

It will be noted that the critical values for the t-test again exceed the corresponding values for the u-test. The t-test is therefore a more conservative test and is recommended for this reason.

Confidence limits

The concept of confidence limits will be illustrated in terms of the first example of the preceding section. In that example $\bar{x}_1 = 16{\cdot}1$ ppm, $\bar{x}_2 = 27{\cdot}3$ ppm, and $s_d = 3{\cdot}51$. The means of the corresponding parent populations were represented by m_1 and m_2. The value of t is given by the expression

$$t = [\bar{x}_1 - \bar{x}_2 - (m_1 - m_2)]/s_d;$$

m_1 and m_2 did not appear in the formula given for t earlier since at that time it was assumed that $m_1 = m_2$. The number $t_{0{\cdot}975} = 2{\cdot}02$ was obtained in such a way that the probability that the calculated t will fall between $-t_{0{\cdot}975}$ and $t_{0{\cdot}975}$ is 0·95. A little algebra shows that this statement is equivalent to saying that the probability is 0·95 that the following statement is true:

$$\bar{x}_1 - \bar{x}_2 - t_{0{\cdot}975}s_d < m_1 - m_2 < \bar{x}_1 - \bar{x}_2 + t_{0{\cdot}975}s_d.$$

In the example under consideration, the corresponding *confidence interval*, as it is called, is $4{\cdot}1 < m_2 - m_1 < 18{\cdot}3$, a result obtained by multiplying the above equation through by -1 since $\bar{x}_1$ is less than $\bar{x}_2$. The probability that this statement is true is 0·95, or, in other words, if this method is used repeatedly, in about 95% of the cases the confidence interval obtained will cover $m_2 - m_1$. It is not correct to say that the probability is 0·95 that $m_2 - m_1$ will fall in the confidence interval since $m_2 - m_1$ is a constant and either falls in a given confidence interval with probability 1 or does not fall in it with probability 0. The confidence interval varies from experiment to experiment and may be expected to cover $m_2 - m_1$ 95% of the time.

A 99% confidence interval may be obtained by replacing $t_{0{\cdot}975}$ by $t_{0{\cdot}995} = 2{\cdot}70$. The resulting interval is $1{\cdot}7 < m_2 - m_1 < 20{\cdot}7$, and, as was to be expected, the increased certainty that the interval covers $m_2 - m_1$ is obtained at the expense of a longer interval. The u-test also leads to a confidence interval if $t_{0{\cdot}975}$ is replaced by $u_{0{\cdot}975} = 1{\cdot}96$. The interval obtained is $4{\cdot}3 < m_2 - m_1 < 18{\cdot}1$ which is slightly shorter than the corresponding 95% confidence interval obtained by the t-test. If the number of degrees of freedom $n_1 + n_2 - 2 = 41$ were smaller the difference between the lengths would be greater, but the interval obtained by means of the u-test should not be used since it is based upon the fallacious assumption that u is normally distributed whereas it actually follows the t-distribution.

If a shorter confidence interval is desired, it may be obtained by increasing the number of observations. For the length of the 95% confidence interval is $2t_{0{\cdot}975}s_d$ and both $t_{0{\cdot}975}$ and s_d tend to decrease as the number of observations increase. In particular, for a given number of observations, it is desirable to take $n_1 = n_2$ since the sum of the reciprocals of these quantities is a minimum when this is the case.

It is assumed in the above discussion that the samples are drawn from populations with equal standard deviations. If this is not the case, a reasonable approximation to a 95% confidence interval can be obtained by replacing $t_{0.975}$ by the t' of the previous section.

This same approach may be used to obtain a confidence interval for either m_1 or m_2. For m_1 the appropriate inequalities for a 95% confidence interval are

$$\bar{x}_1 - \sqrt{w_1} \cdot t_{0.975} < m_1 < \bar{x}_1 + \sqrt{w_1} \cdot t_{0.975}.$$

Still using the data of the first example in the preceding section,

$$s_1^2 = 1128{\cdot}4/12 = 94{\cdot}0, \; s_1^2/n_1 = 94{\cdot}0/13 = 7{\cdot}23 = w_1, \; \sqrt{w_1} = 2{\cdot}69,$$

and $t_{0.975} = 2{\cdot}18$ with 12 degrees of freedom. The 95% confidence interval for m is $16{\cdot}1 \pm 5{\cdot}9$, or 10·2 to 22·0. In other words there is 0·95 probability that the range 10·2 to 22·0 contains the true mean lead content, as distinct from the sample mean of 16·1 ppm.

Finally, we obtain a confidence interval for m_0 whose value we estimated by x_0 in the section on analyzing. To do so we rewrite a formula given by Mood (p. 301) and obtain

$$x_0 - s_{x_0} t_{0.975} \leqq m_0 \leqq x_0 + s_{x_0} t_{0.975}$$

as a 95% confidence interval for m_0. The number of degrees of freedom associated with $t_{0.975}$ is $m + n - 3$. Applying this result to the gallium example in the section on analyzing, the interval is found to be the interval 1·41 to 1·57. This interval is computed from not only the values in the sample but also from those that went into the calibration curve. It is pointed out by Eisenhart (1939) and Mood (p. 299) that this method is valid only if we recalibrate before taking each sample.

An Application

A recent paper by Fairbairn, Ahrens and Gorfinkle (1953) gives data on the trace-element content of many samples of Ontario diabase. Histograms are plotted for each element, showing the distribution in Nipigon-type diabase and in all other diabases (Nipissing, post-Nipissing, Matachewan). With some elements there is a striking difference between the two histograms, and it is most marked with rubidium and potassium. It appears that the Rb and K content of Nipigon diabase is lower than the others, or as stated by the authors: "—correlation between rubidium and potassium—both low in the Nipigon, both high in the Nipissing" (*ibid.*, p. 40). This conclusion suggests the Nipigon rocks may be fundamentally different from the others, and it is of interest to find how different. The problem will be approached by way of the null hypothesis and the t-test.

Taking rubidium first, there were 28 samples of non-Nipigon diabase and 11 of Nipigon type. The figures below have been calculated from the authors' data, using the same symbols as in the preceding section.

$n_1 = 28$	$n_2 = 11$
$\bar{x}_1 = 143{\cdot}6$ ppm	$\bar{x}_2 = 35{\cdot}69$ ppm
$s_1^2 = 7674{\cdot}00$ with 27 degrees of freedom (d.f.)	$s_2^2 = 91{\cdot}75$ with 10 d.f.

It is found that $F = 83{\cdot}6$. From the tables it is found that $F_{0{\cdot}995} = 5{\cdot}12$ (approximately). The hypothesis that the standard deviations are the same must be rejected and the modified t-test is carried out. It is found that $s_d = 16{\cdot}81$ and $\bar{x}_1 - \bar{x}_2 = 107{\cdot}91$, hence $t = 6{\cdot}42$. From the tables the values of t_1 and t_2 for a 1% test are 2·77 and 3·17 respectively. Since t' will fall between these two values it is clear that the calculated t exceeds the 1% level. In other words there is less than 1% probability that the parent populations are the same.

Treating potassium in the same way, there are 28 observations for the non-Nipigon diabases and 9 for the Nipigon type. The data is as follows

$$n_1 = 28 \qquad n_2 = 9$$
$$\bar{x}_1 = 9450 \text{ ppm} \qquad \bar{x}_2 = 3322 \text{ ppm}$$
$$s_1^2 = 23365554 \qquad s_2^2 = 769610$$

Again the F-test is not satisfied, and the modified t-test gives a value $t = 6{\cdot}39$. Using a 1% test the values of t_1 and t_2 are 2·77 and 3·36 respectively. It is clear that the calculated value of t exceeds the 1% level.

Thus from these tests it is possible to say that there is more than 99% probability that the difference in composition between the two kinds of diabase is real.

Conclusions

The conclusion is simple, namely that the application of statistical methods can be of considerable value to geochemists; to be more positive, progress in quantitative geochemistry will be difficult until statistical methods are in more general use. It is perhaps significant that geochemists are (naturally) more familiar with chemistry than with biology; if the reverse had been the case statistical theory would have been applied earlier. However a word of warning is necessary. The tests described in this paper will detect differences; they will give no reason for the difference, for that is a geochemical problem. Statistical theory has no interest in geochemistry, only in the distribution of observations. For this reason one cannot look to statistics for new ideas in geochemistry. The new ideas must come from elsewhere and then the statistics can be used to test them. For example, the application of discrimination tests showed in the last section that the Nipigon diabases of Ontario differ in their rubidium and potassium content from other Ontario diabases. The reason for this difference is however a problem to be answered by petrological argument.

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Argonbestimmungen an Kalium-Mineralien

III. Vergleichende Messungen nach der Kalium-Argon- und Uran-Helium-Methode*

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ABSTRACT

In previous papers measurements were reported about the argon-content of potassium chloride from Buggingen (Valley of the Rhine). The variation of the argon-content with crystal size was shown to be due to a body-diffusion. In addition, we now determined the uranium- and helium-content of the same samples. The helium-content shows a dependence on crystal size similar to the argon-content. By theoretical considerations we came to the conclusion that the salt layers were formerly at a higher temperature than to-day. Under this assumption the diffusion coefficients were evaluated for argon and helium in potassium chloride by combining all results. The new value for the age of the samples (Lower Oligocene) is $(25\ ^{+5}_{-3}) \cdot 10^6 a$. This value is only slightly higher than the previous one $21 \cdot 10^6 a$, which shows that the influence of a varying temperature does not effect the result considerably.

Die beiden vorhergehenden Veröffentlichungen (Gentner, Präg und Smits, 1950 und 1953) beschäftigten sich mit dem quantitativen Nachweis des Argons in Kalisalzen. Nach Kontrolle der Luftargonwerte durch massenspektrometrische Untersuchungen der beim Aufschluß von wasserlöslichen Kalisalzen anfallenden Argonmengen konnte die Meßmethode soweit verbessert werden, daß Unterschiede der Argonkonzentrationen in den einzelnen an sich gleich alten Salzschichten eines tertiären Lagers sicher zu bestimmen waren. Der mit der mittleren Kristallgröße der einzelnen Schichten ansteigende Argongehalt konnte, nachdem andere Möglichkeiten ausschieden, nur so erklärt werden, daß verschieden große Diffusionsverluste für die einzelnen Kristallgrößen eingetreten waren. Die unter der Annahme einer Volumendiffusion berechneten Gehalte an radiogenem Argon 40 stimmten in den Fehlergrenzen mit den experimentellen Werten überein. Bei Berücksichtigung der Diffusionsverluste ergab sich für das oligozäne oberrheinische Kalisalzlager ein Alter von etwa 21 Mill. Jahren.

Die Diffusionsvorgänge hängen nun sehr stark von der Gesteinstemperatur während der Lagerzeit ab. Die vorläufige vereinfachende Annahme, daß die heutige Temperatur des Lagers von 38° C für die ganze geologische Lagerzeit die gleiche gewesen sei, bringt eine Unsicherheit in das errechnete Ergebnis. Es war schon darauf hingewiesen worden, daß bei einer höheren Anfangstemperatur des Lagers ein um etwa 25% höheres Alter sich ergeben könnte.

Zur Klärung dieser noch offenen Frage und zur Kontrolle des Kalium-Argon-Verfahrens wurde an dem gleichen Material auch eine absolute Altersbestimmung nach der Uran-Helium-Methode durchgeführt. Die experimentellen Schwierigkeiten bei dieser Uran-Helium-Methode sind bedeutend größer, weil bei den Salzen nur ungefähr zwei Größenordnungen kleinere Heliummengen nach ähnlichen Messungen von Strutt (1908), Paneth (1928), Karlik (1950) u.a. zu erwarten

* Herrn Professor Dr. Otto Hahn zum 75. Geburtstag in Verehrung gewidmet.

waren. Insbesondere aber ist die quantitative Bestimmung der außerordentlich kleinen Uran-Thorium-Verunreinigungen mit einem erheblichen Fehler behaftet, so daß bei Anwendung der Uran-Helium-Methode mit einer größeren Ungenauigkeit in der Altersangabe gerechnet werden muß. Trotzdem ist ein zweites, unabhängiges Verfahren von großem Wert, um noch mehr Aufschluß über die geologische Geschichte des Lagers zu erhalten.

1. Messmethode

Die in der ersten Veröffentlichung von Smits und Gentner (1950) beschriebene Argonbestimmungsapparatur mußte für die Heliummessungen erheblich erweitert werden. Vor allem eine saubere Trennung des Heliums vom Argon und eine extreme Reinheit des zu messenden Heliums traten als neue experimentelle Probleme zu den bisherigen. Die Abtrennung des Argons vom Helium wurde während des Versuches durch eine spektroskopische Reinheitsprüfung des Heliums dauernd kontrolliert. Zur Durchführung der Messung diente die in Abbildung 1 gezeigte Apparatur*. Der Aufschlußteil ist im wesentlichen der gleiche wie bei der bisherigen Argonapparatur. Nach Reinigung der Edelgase mit dem Calcium- und Kupfer-Kupferoxyd-Ofen wird in einem Kohleröhrchen das Argon durch gekühlte Aktivkohle (−180°C) adsorbiert.

Bei der Durchführung der Methode hat sich herausgestellt, daß die kleinen Gasmengen nur einwandfrei bei Verwendung von Quecksilberabschlüssen und Vermeidung von Fettschliffen gemessen werden können.

Die quantitative spektroskopische Reinheitsprüfung gelang in Kapillaren von 0.5 mm ϕ mit Hochfrequenzanregung. Die gleichzeitig auftretenden Quecksilberlinien konnten dabei als Vergleichsintensitäten herangezogen werden. 2% Verunreinigungen des Heliums wurden noch einwandfrei nachgewiesen.

Für die kleinsten zur Messung gelangenden Gesamtheliummengen von etwa 10^{-5} cm^3 muß nach Kontrollen mit reinem Helium mit einem Fehler $\leq 20\%$ gerechnet werden. Durch Verbesserung des McLeod-Manometers konnten wir diesen Fehler inzwischen unter 10% herabdrücken.

Ebenso wie bei den Argonmessungen ist zu erwarten, daß bei den Heliumbestimmungen ein gewisser Anteil von Lufthelium vorhanden ist, der nicht vom radioaktiven Zerfall stammt. Eine massenspektrometrische Analyse würde in diesem Fall nichts helfen. Wir haben daher angenommen, daß das Verhältnis von Luftargon zu Lufthelium im Salz dem Verhältnis in der Atmosphäre entspricht. Dann liegt der Luftheliumgehalt innerhalb unseres Meßfehlers.

2. Messung des Uran-Thorium-Gehaltes der Kalisalze

Zu der genauen Heliumbestimmung gehört eine quantitative Messung des Uran-Thorium-Gehaltes, die bei den vorliegenden kleinen Mengen auf außerordentliche Schwierigkeiten stößt. Für diese Analyse schien uns die Methode des Nachweises der α-Spuren mit photographischen Kernplatten am besten geeignet. In einer Arbeit von Buttlar und Houtermans (1951) ist die quantitative Bestimmung von Thorium zu Uran geprüft worden. In ähnlicher Weise hat im hiesigen

* Für eine genaue Beschreibung des Verfahrens und der Apparatur vgl. Goebel, Messung des Heliumgehaltes an Kalisalzen zur Altersbestimmung, Diss. Freiburg/Br. 1953.

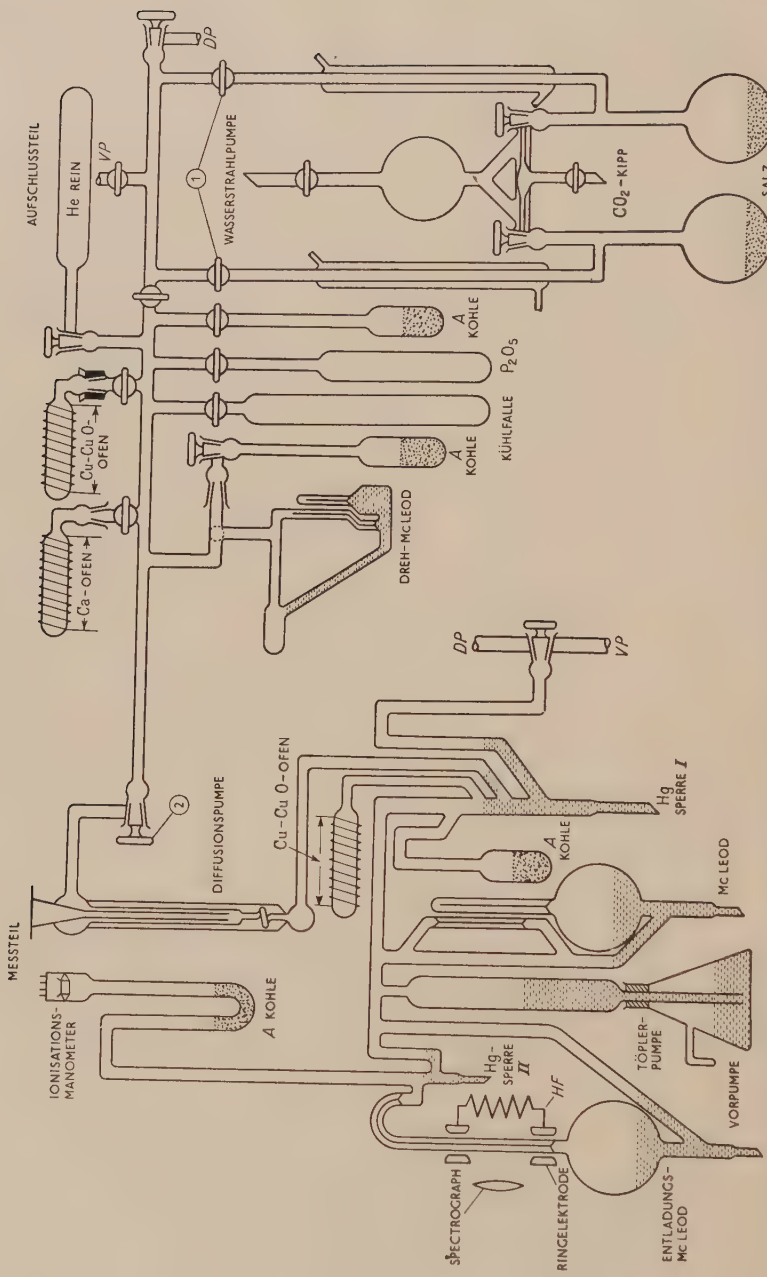

Abb. 1. Vakuumapparatur zum Nachweis kleinster Heliummengen. Im Aufschlußteil (rechts) die beiden Kolben für den Vakuumaufschluß mit luftfreiem Wasser; daneben für die Edelgasreinigung Ca- und Cu/CuO-Ofen, Aktivkohle, P_2O_5-Röhrchen und Kühlfalle. Über die Diffusionspumpe und 2 gelangt das gereinigte Gas in den Meßteil (links).

Institut Frl. KRAFT durch Auflegen von Salzschliffen auf die Photoplatten das Uran-Thorium-Verhältnis gemessen.

Der Urangehalt wurde in der Größenordnung von 10^{-7} g U pro Gramm Salz gefunden. Für das Uran-Thorium-Verhältnis ergab sich ein Wert von 0,15. Die einzige Bestimmung, die an ähnlichem Material vorliegt, stammt von KEMÉNY (1941) und beschäftigt sich nur mit dem Urangehalt von Steinsalzen. Die dabei angewandte Fluoreszenzmethode ergab einen wesentlich tieferen Wert von ca. 10^{-10} g U pro Gramm Salz. Ein Vergleich mit unseren Ergebnissen ist kaum möglich, da es sich dabei um ganz verschiedene Salzlager handelt.

Ist das Uran-Thorium-Verhältnis wenigstens ungefähr bekannt, so kann man aus der Zahl der α-Teilchen, die von einem Volumenelement Salz ausgesandt werden, die im Salz pro Jahr erzeugte Heliummenge berechnen. Dieser Heliumerwartungswert der Schichten ist in Tabelle 1 aufgeführt. Die Aktivität ist, wie aus der Tabelle hervorgeht, für die feinkörnigen heliumarmen Ca*— und Cb-Schichten etwas größer, jedoch liegen die Unterschiede noch in der Fehlerbreite der ausgezählten α-Spuren.

Tabelle 1. *Helium-Erwartungswert aus dem Uran-Thorium-Gehalt der Kalisalze*

Salz-schicht	α/cm^2	cm^3 He *pro Gramm und Jahr*
Eo	160 ± 30	$5{,}0 \cdot 10^{-14}$
Ca	210 ± 35	$6{,}5 \cdot 10^{-14}$
Cb	240 ± 45	$7{,}4 \cdot 10^{-14}$

Bestrahlungsdauer $t = 1{,}8 \cdot 10^6$ sec

3. Ergebnisse der Heliumbestimmungen

Die hier mitgeteilten Messungen beziehen sich auf dieselben Salze, die seinerzeit bereits auf Argon von uns untersucht worden waren, und deren Argongehalte in der zweiten Veröffentlichung (GENTNER, PRÄG und SMITS, 1953) in Tabelle 1 mitgeteilt wurden. Nachfolgende Tabelle 2 enthält die Ergebnisse unserer Heliumbestimmungen. Gleichzeitig wurde auch der Argongehalt der Salze zur Kontrolle nochmals bestimmt; die erhaltenen Werte des radiogenen Argon 40 sind in der letzten Spalte der Tabelle 2 aufgeführt. Die Schwankungen der für die einzelnen Schichten aus der Zahl der α-Spuren ermittelten Heliumerwartungswerte bleiben, wie oben ausgeführt, innerhalb der Fehlerbreite, weshalb für alle Schichten mit einem Durchschnittswert von $6 \cdot 10^{-14}$ cm^3 pro Gramm Salz und Jahr gerechnet wurde. Die mittlere Kristallgröße bestimmten wir, wie früher beschrieben, an Dünnschliffen der Salze.

In der zweiten Veröffentlichung beschäftigten wir uns auch eingehend mit den bei den Salzen auftretenden Störungen des Kristallaufbaues. Man entdeckte bei den Schichten Bi und Bg unter dem Mikroskop kleine Hohlräume, die in ganzen Ebenen den Kristall durchziehen (GENTNER, PRÄG und SMITS, 1953, Abb. 6). Gerade für diese Kristalle, die wohl ursprünglich in den Störebenen getrennt waren, also heute eine zu große mittlere Kristallgröße zeigen, stellten wir ebenfalls wesentliche Abweichungen des Heliumgehaltes der Schichten von dem sonst mit der Kristallgröße gleichmäßig verlaufenden Edelgasgehalt fest. Diese Parallelität

* Bezeichnung der wechselnden Steinsalz- und Sylvinschichten nach STURMFELS.

der Ergebnisse der Helium- und Argonmessungen kann als Beweis für die Richtigkeit unserer früheren Annahmen angesehen werden. Im Normalfall ist also für den Helium- und Argongehalt ein stetiges Anwachsen mit der Kristallgröße der Salze gegeben. Die Unterschiede der Konzentrationen in den fein- und grobkristallinen Schichten sind für das Helium grösser als für das Argon.

Tabelle 2. Helium- und Argongehalt der Bugginger Kalisalze

Probe	*Kristallgröße cm*	*He/g Salz* $\cdot 10^7$ *cm³*	$A^{40}/100\ g\ K$ $\cdot 10^3$ *cm³*
201 Eo	0,18	7,80	6,57
202 Eo		7,06	6,57
206 Eo		6,23	6,92
207 Eo		6,43	6,68
— Ei	0,13	5,75	—
203 Ca	0,065	4,98	4,08
204 Ca		4,75	3,76
205 Ca		3,22	3,80
213 Ca		4,49	—
214 Ca		4,41	3,52
222 Bn	0,07	3,44	—
225 Bn		3,26	—
230 Cb	0,04	1,61	3,23
231 Cb		1,33	3,03
— Ca		1,95	—

Legen wir einer Überschlagsrechnung einen Heliumerwartungswert von $5 \cdot 10^{-14}$ cm³ pro Jahr und Gramm und eine durchschnittliche Heliumkonzentration von $5 \cdot 10^{-7}$ cm³ pro Gramm zugrunde, so erhalten wir zunächst ein "Heliumalter" von nur 10 Mill. Jahren. Berücksichtigt man jedoch die eingetretenen Diffusionsverluste, so kann, wie noch im folgenden zu zeigen ist, der Unterschied in der Altersbestimmung nach der Uran-Helium- bzw. Kalium-Argon-Methode erklärt werden.

4. Berücksichtigung der Diffusion der Edelgase

Den Berechnungen des Diffusionsverlustes an Argon war früher die Annahme zugrundegelegt worden, daß die Temperaturverhältnisse während der Lagerzeit der Sylvine konstant waren. Diese Annahme läßt sich nicht mehr aufrechterhalten, wenn man die Heliumwerte in gleicher Weise deuten will. Die Kristallgrößenabhängigkeit müßte für das Helium dann nämlich viel größer sein als tatsächlich gefunden wurde. Bisher waren für einen veränderlichen Temperaturverlauf keine Anhaltspunkte gegeben. Nimmt man aber an, daß das Sylvinlager im Laufe der Zeit eine Temperaturänderung erfahren hat, so lassen sich die experimentellen Helium- und Argonwerte theoretisch deuten. Da der Diffusionskoeffizient sehr stark von der Temperatur abhängt, wird hiernach auch dieser eine Funktion der

Zeit sein. Der Vorgang der Diffusion und die gleichzeitige radiogene Entstehung der Edelgase unterliegen somit der Differentialgleichung mit den weiter unten angeführten Bezeichnungen:

$$\frac{\partial c}{\partial t} = D(t) \cdot \triangle c + \lambda_K c_{K_0} e^{-\lambda t}$$

Wie auch bei den in unserer vorigen Veröffentlichung erwähnten Rechnungen, können wir uns auf die Näherung

$$\frac{\partial c}{\partial t} = D(t) \cdot \triangle c - \lambda c + \lambda_K c_{K_0}$$

im Fall des Argons und

$$\frac{\partial c}{\partial t} = D(t) \cdot \triangle c - \lambda c + 8\lambda c_{U_0}$$

im Fall des Heliums beschränken, wenn man die Entstehung von 8 Helium-Atomen aus 1 Uran-Atom (Thorium = 7 Helium-Atome) berücksichtigt.*

Nehmen wir einen näherungsweise linearen Abfall der Temperatur ($T = T_0(1-\beta t)$) im Bugginger Lager an, so erhalten wir unter der berechtigten Voraussetzung $\beta t \ll 1$ für D in erster Näherung:

$$D = D_{t_0} e^{-bt}$$

Unter Verwendung dieser zeitlichen Abhängigkeit des Diffusionskoeffizienten ergibt die Integration der obigen Differentialgleichung und nachherige räumliche Mittelung über die Edelgaskonzentration bei Einführung geeigneter Vernachlässigungen

$$\bar{c} = \frac{B}{b} \sum_{n_i=0}^{\infty} \left[e^{\xi_t^{n_i}} \int_{\xi_t^{n_i}}^{\xi_0^{n_i}} \frac{e^{-\xi}}{\xi} d\xi \prod_{i=1}^{3} \mathrm{K}_{n_i}^2 \right]$$

mit

$$B = \left(\frac{8}{\pi^2}\right)^3 \lambda_K c_{K_0} \qquad \text{für Argon,}$$

$$B = \left(\frac{8}{\pi^2}\right)^3 8\lambda c_{U_0} \qquad \text{für Helium,}$$

$$\xi_t^{n_i} = \sum_{i=1}^{3} (2n_i + 1)^2 \frac{\pi^2}{d^2} \frac{D_{t_0}}{b} e^{-bt}$$

$$\mathrm{K}_{n_i} = \frac{1}{2n_i + 1}$$

c = Edelgaskonzentration für (x_i, t)

$\bar{c}$ = mittlere Edelgaskonzentration zur Zeit t

$D(t)$ = Diffusionskonstante zur Zeit t

λ_K = Zerfallskonstante des K-Zerfalls von K^{40}

λ = Zerfallskonstante von Kalium bzw. Uran/Thorium

c_{K_0} = Konzentration des Kaliums für $t = 0$

* Vgl. Präg, Berücksichtigung der Diffusion der Edelgase bei Altersbestimmungen nach der Kalium-Argon- und Uran-Helium-Methode, Diss. Freiburg/Br. 1953.

c_{U_0} = Konzentration des Urans für $t = 0$

β = Temperaturänderung pro Jahr

b = Exponentialkoeffizient für den Abfall der Diffusionskonstante

n_i = Laufzahltrippel

d = mittlere Kristallgröße

Führt man noch

$$D_t = D_{t_0} e^{-bt}$$

ein, so läßt sich dies ganz allgemein in der Form

$$\bar{c} = E_{\mathrm{Ar}} f(D_{t_0\mathrm{Ar}},\ D_{t\mathrm{Ar}},\ d,\ t)$$

oder

$$\bar{c} = E_{\mathrm{He}} f(D_{t_0\mathrm{He}},\ D_{t\mathrm{He}},\ d,\ t)$$

schreiben, wobei E_{Ar} der Argon-Erwartungswert ($1{,}22 \cdot 10^{-14}$ mm³ Ar^{40}/100 g K·sec bei 3,3 K-Zerfällen/g K·sec) und E_{He} der oben angegebene Helium-Erwartungswert in cm³ pro Gramm Salz und sec ist. Die numerische Auswertung dieser Funktion gestattet, den theoretisch zu erwartenden Zusammenhang zwischen Edelgasgehalt und Kristallgröße in Abhängigkeit vom Alter der Salze und dem Anfangs- und Endwert des Diffusionskoeffizienten (D_{t_0}, D_t) anzugeben. Aus der allgemeinen Darstellung entnimmt man, daß bereits drei Heliummeßwerte die Größen $D_{t_0\mathrm{He}}$, $D_{t\mathrm{He}}$ und t, d.h. Temperaturverlauf und Alter eindeutig festlegen. Unter der durchaus berechtigt erscheinenden Annahme, daß der Diffusionskoeffizient des Argons nahezu gleiche Temperaturabhängigkeit aufweist wie der des Heliums, legt ein einziger weiterer Argon-Meßwert auch Anfangs- und Endwert des Argon-Diffusionskoeffizienten ($D_{t_0\mathrm{Ar}}$, $D_{t\mathrm{Ar}}$) fest.

Man kann sich bei den Berechnungen auf positives β und b beschränken*, wonach sich die gegebene Gleichung auch in der Form

$$\bar{c} = \frac{B}{b} \sum_{n_i=0}^{\infty} \left[e^{\xi_t^{n_i}} \{ E_i(-\xi_0^{n_i}) - E_i(-\xi_t^{n_i}) \} \prod_{i=1}^{3} \mathrm{K}_{n_i}^2 \right]$$

schreiben läßt. Die nur für positive ξ-Werte definierte Exponential-Integral-Funktion E_i findet man in den "Tafeln höherer Funktionen" von Jahnke-Emde und in den "Tables of Sine, Cosine and Exponential Integrals" vertafelt.

In Abbildung 2 ist die Abhängigkeit des Edelgasgehaltes von der Kristallgröße graphisch wiedergegeben. Der eingetragene Ordinatenmaßstab $\bar{c}$ ist, wie angegeben, auf Argon- und Heliummeßwerte umzurechnen. Den eingezeichneten theoretischen Kurven, die den experimentell ermittelten Werten am besten entsprechen, liegen folgende Werte zugrunde:

$$D_{t_0\mathrm{Ar}} = 5 \cdot 10^{-18}\ \mathrm{cm^2/sec}$$

Kurve 1: $D_{t\mathrm{Ar}} = 5 \cdot 10^{-20}\ \mathrm{cm^2/sec}$

$$t = 25 \cdot 10^6 \quad \mathrm{a}$$

$$D_{t_0\mathrm{He}} = 12 \cdot 10^{-18}\ \mathrm{cm^2/sec}$$

Kurve II: $D_{t\mathrm{He}} = 12 \cdot 10^{-20}\ \mathrm{cm^2/sec}$

$$t = 25 \cdot 10^6 \quad \mathrm{a}$$

* Bei Annahme eines negativen β und b verläuft die Kristallgrößenabhängigkeit steiler als für den Wert β, $b = 0$. Tatsächlich haben wir aber für Helium einen flacheren Verlauf gefunden als bei konstanter Temperatur zu erwarten wäre.

Zusammenfassend scheint uns folgendes Ergebnis für die Richtigkeit unserer Annahmen zu sprechen. Wenn durch eine Meßreihe die Kristallgrößenabhängigkeit des Argons ermittelt ist, muß nach unseren Voraussetzungen ein einziger Heliumwert den Verlauf der Kristallgrößenabhängigkeit des Heliums festlegen. Tatsächlich fallen die experimentellen Werte mit dieser theoretisch vorausberechneten

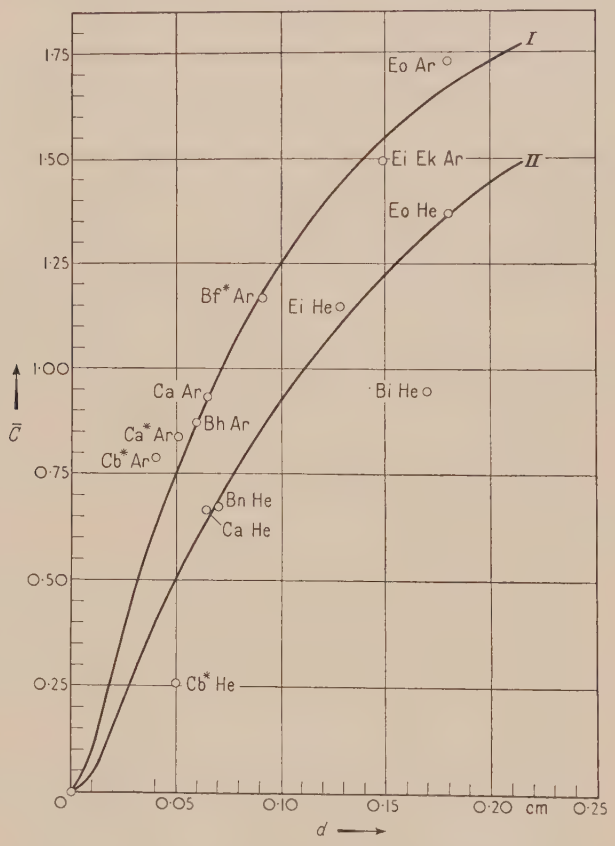

Abb. 2. Edelgasgehalt in Abhängigkeit von der Kristallgröße. Eingezeichnete Punkte: experimentelle Werte. Um die Ar-Konzentration ($\bar{c}$Ar) in mm³ Ar^{40}/100 g K zu erhalten, hat man die Ordinatenwerte mit 3,85 zu multiplizieren. Die mittlere He-Konzentration ($\bar{c}$He) in cm³/g Salz errechnet sich aus dem Produckt von $5 \cdot 10^{-7}$ und dem Ordinatenwert. Die Bezeichnungen BiHe, CaAr, etc. bedeuten, daß der Meßpunkt die Helium- bzw. Argon-Konzentration der Bi- bzw. Ca-Kalisalzschicht (nach STURMFELS) wiedergibt. Mit Ausnahme der mit* bezeichneten Meßpunkte (Kalisalze aus dem Elsaß) handelt es sich ausschließlich um Salze des Bugginger Kalireviers.

Heliumkurve zusammen. Den für die Diffusionskoeffizienten gefundenen Werten kann natürlich keine allzu große Genauigkeit beigemessen werden, da sich die den Meßwerten anhaftenden Fehler in weit stärkerem Maße auf die Diffusionskonstanten übertragen. Berücksichtigt man alle Fehlermöglichkeiten, so kann man die erhaltenen Werte folgendermaßen zusammenfassen:

$$D_{Ar}(40°C) = (\ 8 \pm 7\ ) \cdot 10^{-20}\ \mathrm{cm^2/sec}$$

$$D_{He}(40°C) = (20 \pm 16) \cdot 10^{-20}\ \mathrm{cm^2/sec}$$

Dies entspricht einem Temperaturabfall von

$$(70 \pm 30)°C \text{ auf } 40°C$$

und einem Alter von

$$t = (25\ ^{+5}_{-3}) \cdot 10^6\ a.$$

5. Diskussion

Unter Berücksichtigung der Diffusion lassen sich die zunächst auseinanderfallenden Ergebnisse der Uran-Helium- und Kalium-Argon-Methode in Übereinstimmung bringen, wenn angenommen wird, daß die Diffusionskonstante des Heliums größer ist als die des Argons und daß die Temperatur des Lagers in früheren Zeiten höher war als heute.

Diese Ergebnisse entsprechen durchaus den Erwartungen, die man in dieser Hinsicht treffen kann. Denn auf Grund seiner geringeren Atommasse und daher höheren Molekulargeschwindigkeit ist es leicht zu verstehen, daß dem Helium ein größerer Diffusionskoeffizient zukommt als dem Argon. Wäre allein das Verhältnis der Molekulargeschwindigkeiten für den Unterschied der Diffusionskoeffizienten verantwortlich, so sollte man für das Verhältnis der Diffusionskoeffizienten einen Wert von 3,16 erwarten. Unser Wert von 2,5 stimmt mit diesem theoretischen Wert innerhalb der Fehlergrenzen überein. Auch ein kleiner Unterschied wäre infolge verschiedener Wirkungen der Molekülkräfte verständlich.

Der von uns als Diffusionskoeffizient errechnete Wert von D stellt wahrscheinlich eine sehr komplexe Größe dar. Es kann nicht angenommen werden, daß in den untersuchten Salzkristallen eine reine Volumendiffusion, wie sie nur im Einkristall stattfindet, vorliegt, da bei den natürlich gewachsenen Kristallen mit Verunreinigungen, Fehlstellen und kleinsten Strukturstörungen gerechnet werden muß. Wahrscheinlich setzt sich der Diffusionsvorgang zusammen aus reiner Volumendiffusion, Fehlstellenwanderung und Verschiebung der Gasatome entlang innerer Störgebiete.

Eine zeitlich fallende Temperatur entspricht ebenfalls unseren schon früher dargelegten Vorstellungen einer Abkühlung des Lagers seit der Zeit des Kaiserstuhl-Vulkanismus. Wenn auch eine in Einzelheiten gehende Aussage über den Temperaturverlauf nicht möglich ist, so kann es doch als sicheres Ergebnis angesehen werden, daß in erster Näherung eine stetige Abkühlung des Lagers stattfand.

Das durchweg befriedigende Ergebnis der durchgeführten Betrachtungen deutet darauf hin, daß die dargelegte Abhängigkeit des Edelgasgehaltes von der Kristallgröße in erster Linie auf Diffusionsvorgänge zurückzuführen ist. Andere Faktoren, die eine solche Erscheinung hervorgerufen haben könnten, dürften nur von zweitrangiger Bedeutung gewesen sein.

Für eine absolute Altersangabe ist aber außerdem entscheidend, ob die heute anzutreffenden Verhältnisse primärer Natur sind. Wir haben schon früher darauf hingewiesen, daß als Alter der Salze nach den beiden Methoden nur die Zeitspanne ermittelt werden kann, in der die "Edelgasuhr" ihren Lauf ohne Unterbrechung bis heute fortsetzen konnte. Es läßt sich aber zeigen, daß geologische Ereignisse, die einen völligen Verlust der Edelgase zur Folge gehabt hätten, bald nach der primären Entstehung der Salzlager eingetreten sein müßten. Aus der Zeit nach dem Kaiserstuhl-Vulkanismus ist ein solches Ereignis nicht bekannt und der Vulkanismus selbst wird höchstens für eine Temperaturerhöhung im Lager verantwortlich gemacht werden können. Es haben nämlich die im Bugginger Revier angetroffenen Ankaratritvorkommen (Hasemann, 1951) nur einen kleinen Teil des Lagers direkt beeinflußt, und nur in einem begrenzten Umkreis wurden Vertaubungen und chemische Veränderungen des Kaliflözes hervorgerufen.

Für die Möglichkeit einer primären Abscheidung der verschiedenen Schichten gibt es mehrere Hinweise. So bestätigt LOTZE (1938), daß "bei gleichförmigen Schicksal der Lagerstätte horizontmäßige Unterschiede wohl primär sedimentär sein können." Die grobkernigen Schichten zeigen ein lockeres Gefüge und in manchen Schichten wird eine Ausrichtung der Kristalle, die nach STURMFELS (1943) ursprünglich sein soll, beobachtet. Ebenso läßt FULDA (1935) die Möglichkeit einer Erhaltung des ursprünglichen Wechsels von grob- und feinkristallinen Lagern durchaus zu. WAGNER (1926) und auch LOTZE (1938) sehen in der verschiedenen Wassertiefe der ausschiedenden Salzseen reale Gründe für die verschieden große Auskristallisation der Salze. Bleibt somit mindestens die Möglichkeit für die primäre Abscheidung der heutigen Kristallgrößen bestehen, so darf auch umgekehrt aus dem Erfolg der Diffusionsberechnungen der einzelnen Schichten auf deren primäre Entstehung geschlossen werden; denn die Kristallgrößenabhängigkeit des Edelgasgehaltes widerspricht der Annahme ständiger größerer Veränderungen in den Salzschichten.

Wir ordnen daher dem Bugginger Lager unter gleichzeitiger Anwendung der Kalium-Argon- und Uran-Helium-Methode ein Alter von $25\ ^{+5}_{-3}$ Mill. Jahren zu. Angesichts der Unsicherheiten in den Diffusions- und Temperaturfragen wird es wohl kaum möglich sein, diese Fehlergrenze weiter herabzusetzen und dieser Wert muß somit als endgültig betrachtet werden.

Herrn Dr. H. SIMON, dem Direktor der Kaligewerkschaft Buggingen danken wir besonders für die Bereitstellung des Untersuchungsmaterials sowie für die Durchführung der Kalium-Analysen. Im Rahmen seiner Diplomarbeit hat Herr WALTER HUBER einen größeren Teil der Heliummessungen selbständig durchgeführt, wofür wir ihm auch an dieser Stelle unseren Dank aussprechen. Diese Arbeit wurde von der Deutschen Forschungsgemeinschaft unterstützt.

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The occurrence of gallium in blende

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ABSTRACT

The radioactivation method of analysis of Brown and Goldberg for the determination of gallium in meteorites has been developed to provide an accurate procedure for the determination of gallium in blende specimens.

The geochemistry of the occurrence of gallium in blende is discussed, and the available evidence tends to suggest that trivalent gallium substitutes for zinc in the crystal lattice of the mineral.

Gallium is an unusual metal in that it has a very low melting point (*c.* 30°C), and can occur as a liquid at room temperatures, since once melted it remains persistently superfused. In addition its crystal structure is quite exceptional. Owing to its comparative rarity, the commercial application of the metal is limited at the present time, but with the isolation of larger quantities it will probably assume considerable practical importance.

In the lithosphere traces of gallium occur widely disseminated in silicate minerals, in which its mode of occurrence is largely governed by camouflage by aluminium, the radii and ionisation potentials of the Ga^{3+} and Al^{3+} ions being similar (Ga^{3+} $r = 0{\cdot}62$ Å, $I = 30{\cdot}7$ v; Al^{3+} $r = 0{\cdot}51$ Å; $I = 28{\cdot}44$ v). Unlike aluminium, however, gallium has quite a strong chalcophile tendency and is found in blende in many parts of the world. According to Oftedal (1940) blende is the only common gallium bearing sulphide mineral, and this fact is borne out by the spectrographic analysis of a wide range of sulphide minerals carried out by the authors.

No minerals with gallium as a major constituent are known, and at the present time the element is largely obtained as a by-product from coke ovens. If there is an increased demand for the element, its determination in blende will probably be of importance, and it is desirable to have an understanding of the geochemical factors governing the occurrence of gallium in the mineral.

Determination of Gallium in Blende by Radioactivation Analysis

Introduction

Many quantitative procedures for the analysis of traces of gallium in mineralogical specimens have been described. A discussion of all the methods would be out of place here, but mention will be made of some of the more accurate modern methods.

Oftedal (1940) has determined gallium together with other trace elements in Norwegian blendes by spectrochemical analysis employing the carbon arc cathode-layer method, the zinc of the blende being used as an internal standard.

Gabrielson (1945) has similarly analysed a large number of Swedish blendes for various trace elements including gallium. Like Oftedal he used a spectrographic method employing the D.C. arc, with zinc as internal standard for gallium. The line pair employed by Gabrielson, however, was different from that utilised by Oftedal.

A very similar problem has been investigated by Strock (1945), who has studied the determination of various trace elements in zinc sulphides. Beryllium was used as internal standard.

Ahrens has determined gallium in various silicate rocks and minerals, and gallium is included in the analytical scheme worked out by Ahrens (1951) for the complete quantitative spectrochemical analysis of a silicate. Indium is used as an internal standard.

Mukherjee (1948) has investigated the spectrographic determination of gallium in Indian bauxite by the carbon arc cathode-layer method. A large number of semi-quantitative spectrochemical methods for determining gallium in minerals have also been described.

Although spectrographic methods have been most widely employed, there are other techniques suitable for determining gallium in mineralogical materials.

Sandell (1947) has determined gallium in silicate rocks by a method based on the fluorescence reaction of gallium with 8-hydroxyquinoline, and Majumidar and Sarkar (1947) have determined it in bauxite by a colorimetric method with quinalizarin.

Brown and Goldberg (1949) have investigated the distribution of gallium in meteorites utilising a radioactivation method of analysis. Numerous analyses by the method have shown that it permits the determination of gallium in the range 0·0001 to 0·01% with a precision of 10% or better. This method has been developed to provide an accurate procedure for the determination of gallium in blende specimens, as described below.

A radioactivation method of analysis has the advantage of extreme sensitivity, and also owing to the possibility of using carriers in the chemical separations, difficulties due to adsorption and contamination are considerably less than in chemical methods for determining microgram and submicrogram quantities. The precision attainable is also often better than that obtained by spectrochemical analysis.

Analysis method

In the present work the Harwell pile was used as a neutron source. Gallium has two stable isotopes Ga^{69} (per cent abundance 60·2) and Ga^{71} (per cent abundance 39·8). On irradiation with thermal neutrons, both isotopes undergo n; γ reactions giving rise to β emitting gallium isotopes.

$$Ga^{69}\ (n;\ \gamma)\ Ga^{70};\ Ga^{70} \xrightarrow{20\cdot3\text{m.}} Ge^{70} + \beta$$

$$Ga^{71}\ (n;\ \gamma)\ Ga^{72};\ Ga^{72} \xrightarrow{14\cdot1\text{h.}} Ge^{72} + \beta$$

The activation cross section for the reaction Ga^{71} $(n;\ \gamma)$ Ga^{72} is 4·5 barns, and the saturation activity of Ga^{72} which is obtainable using the flux of 10^{12} neutrons per sq. cm per sec available in the Harwell pile is $1{\cdot}5 \times 10^{10}$ disintegrations per sec per g of gallium. For an irradiation period of 4·5 h the Ga^{72} activity generated is $3{\cdot}0 \times 10^{9}$ disintegrations per sec per g of gallium.

In determining gallium in blende specimens, the blende samples were washed thoroughly with distilled water followed by acetone, and dried in a jet of compressed air. The cleaned minerals were then wrapped in filter paper and broken down in a hard steel ore crusher. From the broken material, which was examined under high magnification, small homogeneous fragments were separated by hand picking. These were ground down to a fine powder in an agate mortar, with the usual precautions as to the avoidance of contamination.

Samples of *c.* 50 mg of the blendes were placed in thin (2 mm bore) sealed polythene tubes, packed together with cotton wool in a standard aluminium screw-top can 3 in. long by 1 in. in diameter, and irradiated for 4·5 hours in the "self-serve" positions of the Harwell pile. With each batch of blende samples, a standard sample of *c.* 10 mg of gallium 8-hydroxyquinolate was irradiated simultaneously. After removal from the pile, the aluminium can was allowed to "cool" for about an hour. The unknowns and standards were then chemically treated, using a modification of the procedure of Brown and Goldberg (1949). In the case of the blendes, in order to isolate the gallium activity use was made of the fact that gallium, as the trichloride is readily extracted by ether from 5·5 M hydrochloric acid, is not precipitated by H_2S in acid solution, is amphoteric, and can conveniently be precipitated as the 8-hydroxyquinolate.

Spurious gallium from secondary nuclear reactions

In the radioactivation analysis of gallium in blende, allowance must be made for the fact that elements other than gallium on irradiation undergo nuclear reactions leading to the formation of gallium isotopes.

A secondary reaction of this type is Zn^{70} $(n; \gamma)$ $Zn^{71} \xrightarrow{\beta} Ga^{71}$ $(n; \gamma)$ Ga^{72}, whereby Ga^{72} activity is produced from the Zn^{70} isotope. It can be calculated (see Rubinson, 1949) that for a 4·5 h irradiation at a flux of 10^{12} neutrons per sq cm per sec the apparent gallium content of zinc sulphide due to this secondary transformation is only 3×10^{-4} ppm and can hence be ignored in the determination of gallium in blende.

In blendes containing germanium, Ga^{72} activity may be produced by the change Ge^{70} $(n; \gamma)$ $Ge^{71} \xrightarrow{K,\gamma,e^-} Ga^{71}$ $(n; \gamma)$ Ga^{72}. Calculation, however, shows that this transformation is unlikely to affect the radioactivation analysis of gallium in blende specimens. Germanium may also give Ga^{72} activity with fast neutrons (which may be present to an extent of about 10% of the slow neutron flux in the self-serve positions of the Harwell pile) by the reaction Ge^{72} $(n; p)$ Ga^{72}. Since, however, the cross section for the $(n; p)$ reaction on Ge^{72} is likely to be relatively small, and germanium is found only as a trace constituent of blendes, this reaction should not interfere to any important extent.

Other possible nuclear reactions which may give rise to Ga^{72} activity such as—

$$As^{75}\ (n; \alpha)\ Ga^{72}$$

$$Ge^{73}\ (\gamma; p)\ Ga^{72}$$

are likely to be unimportant, and have been ignored in the present work.

Any interference of importance due to the production of radioactive gallium isotopes other than Ga^{72} should be apparent from the energy and decay measurements made on the counted samples from each blende specimen.

Self shielding

Under the irradiation conditions employed, i.e. 50 mg blende samples, and 10 mg gallium 8-hydroxyquinolate standards irradiated in thin polythene tubes, no correction for self shielding differences in sample and standard are necessary.

The chemical separation procedure for gallium in blende

Step 1. The irradiated blende samples were dissolved in about 40 ml of hot concentrated hydrochloric acid, together with about 5 mg of inactive gallium as an isotopic carrier.

Step 2. Small amounts of Cu, Cd, In, and Sb^{III} were added as hold back carriers, and the solution made about 5·5 M in hydrochloric acid. The cold acid solution was then extracted with an equal volume of ether which had been pretreated with concentrated hydrochloric acid. The ether layer was separated and agitated thoroughly with distilled water. The resulting aqueous layer was drawn off and retained.

Step 3. Step 2 was repeated, and ether removed from the final solution by heating on a water bath.

Step 4. After removal of the ether, the solution was acidified with dilute hydrochloric acid and a small amount of Sb^{III} carrier was added. The solution was boiled and H_2S passed through the hot solution. The resulting antimony sulphide scavenging precipitate was filtered and discarded.

Step 5. The filtrate from step 4 was boiled to remove H_2S. A little Fe^{III} carrier was then added, followed by sodium hydroxide until the solution had a hydroxide concentration of 1–2 M, precipitating all the iron present. A drop of aerosol was added, and after centrifuging, the precipitate was discarded. To make sure that the precipitate was completely removed, the solution was passed through a Whatman No. 541 filter paper.

Step 6. The solution was acidified to $p\mathrm{H} = 1$ and heated to 70°C 5 ml of a 1% alcoholic solution of 8-hydroxyquinoline was added, and this was followed by the dropwise addition of 3 M ammonium acetate until precipitation of gallium 8-hydroxyquinolate was complete. The precipitate was separated by centrifuging, washed thoroughly with hot water, followed by ether, and was then ready to be mounted for counting.

Treatment of the gallium standard

The gallium 8-hydroxyquinolate standards irradiated simultaneously with the blende samples were dissolved in hot concentrated hydrochloric acid and the solutions diluted to 100 ml. A 1 ml aliquot was then precipitated with Ga carrier as in the procedure above.

Counting technique

A thin window Geiger-Müller counter was used for measuring the β-activities of the gallium 8-hydroxyquinolate precipitates from both the samples and standard. The precipitates suspended in a little water were transferred with transfer pipettes, a little at a time, to weighed aluminium counting trays. The transferred slurries were then evaporated to dryness under an infrared lamp, care being taken to ensure that the resulting deposits on the trays were uniform. The precipitates on the trays were dried at 110°C for about 15 min, allowed to cool, and the trays reweighed to establish the chemical yield in each case. In order to allow for self absorption, the samples mounted for counting from blendes and standard were of similar weight.

The counting measurements were made over a period of 4 half lives to determine the decay curve in each case. This measurement of decay curves was facilitated in some cases by using a special unit, allowing counting at suitable predetermined intervals automatically. Absorption curves of standards and unknowns were also measured, aluminium absorbers being used. Where conveniently possible, 10,000 counts were taken for each measurement.

All decay curves showed a half life of 14·1 hours, while max β-particle ranges obtained from absorption curves by using the comparison method of Feather (1938) varied from 1650 to *c.* 1800 mg/cm Al, corresponding to a max β-energy of 3·1–3·5 Mev. These data indicated that only Ga^{72} activity was being counted.

Results

In analyses of samples containing between 0·001 and 0·03% gallium, standard deviations fell in the range 1–4%. In some cases the gallium was also determined spectrographically, and the results obtained by the radioactivation and spectrochemical methods showed close agreement. In Table 1 some results of the analysis of gallium in blendes by the radioactivation and spectrochemical procedures are given.

Geochemistry of the Occurrence of Gallium in Blende

The distribution of gallium in blende

Goldschmidt and Peters (1931) and various other workers have shown that gallium is closely associated with aluminium in silicate minerals, and tends to become slightly enriched in the later stages of magmatic differentiation. If deposition of blende occurs, however, it appears that gallium tends to desert aluminium for the sulphide mineral (Graton and Harcourt, 1935).*

This chalcophile character of gallium, as opposed to aluminium, may be due to its capacity to form sulpho-salts (sulphogallates) (Ivanov-emin and Rabovik, 1947) in which respect it is totally distinct from aluminium and resembles other B sub-group elements.

Extensive analyses by various workers (e.g. Papish and Stilson (1930), Goldschmidt and Peters (1931), Graton and Harcourt (1935), Stoiber (1940), Oftedal (1940), Gabrielson (1945), Warren and Thompson (1945), Evrard (1945)) have shown that the gallium content of blende is primarily dependent on the region in which the mineral occurs, but that usually the amount of gallium is

* It is interesting to note that Papish and Stilson (1930) have found that gallium occurs in gahnite, the element in this case being associated with both aluminium and zinc.

highest in blendes of low temperature of formation. The gallium concentration of low temperature blendes is frequently between 0·01 and 0·1%, while blendes formed at intermediate temperatures generally contain <0·01% gallium. The gallium content of high temperature blendes is usually no more than 0·001%.

Table 1. *Percentage gallium in blende specimens determined by radioactivation and spectrochemical analysis*

Mineral locality	Gallium content by radioactivation analysis % Ga	Gallium content by spectrochemical analysis % Ga
Threlkeld mine, Keswick, Cumberland, England	0·019 0·020 0·020 0·020 Av. 0·020	0·022 0·020 0·023 0·021 Av. 0·022
Force Crag mine, Coledale, Keswick, Cumberland, England	0·0055 0·0059 Av. 0·0057	0·0051 0·0051 0·0051 Av. 0·0051
Brandelhow mine, Keswick, Cumberland, England	0·020 0·020 Av. 0·020	0·021 0·020 0·022 0·023 Av. 0·022

The order of these values may be compared with the figure of 0·0015% for the abundance of gallium in igneous rocks, and the value of 0·0002% for the abundance of the element in magmatic sulphides (Rankama and Sahama, 1950).

In Table 2 the range of the gallium concentration in blendes from certain selected regions is given. The data readily indicate the importance of the metallogenic province in determining the gallium content of blende. Thus the blende of the Mississippi Valley deposits is far richer in gallium than that of the somewhat similar European ores, although both are of low temperature formation.

Little information is available on the gallium content of wurtzite. Two specimens from Pribram, Bohemia, analysed by the authors were found to contain <0·0001% Ga.

Nature of the occurrence of gallium in blende

Because GaAs has the blende structure and similar unit cell dimensions to ZnS (GaAs, $a = 5{\cdot}63$ Å; ZnS, $a = 5{\cdot}43$ Å) Goldschmidt and Peters (1931) have suggested that the reason for the occurrence of gallium in blende rather than in other sulphide minerals is that it may be present as the arsenide. Since GaSb and

GaP have the blende structure it has also been suggested that gallium may be present in blende as the antimonide or phosphide. Alternative possibilities are that the element may occur in blende owing to divalent or trivalent gallium entering the lattice position normally occupied by zinc.

Table 2. Gallium content of blendes in various regions

Region	*Temperature type of deposit*	*Range of gallium concentration*	*References*
Cumberland, England	low	Often 0·001–0·03%	[22], [24], [14]
Derbyshire, England	low	0·001–0·01%	[24], [14]
Central Kentucky, U.S.A.	low	generally 0·01–0·1%	[22]
Mississippi Valley, U.S.A.	low	generally 0·001–0·1%	[9], [24]
European Mississippi Valley type (Belgium, Poland, Germany)	low	rarely >0·0001%	[9], [22], [24] [5]
Palaeozoic and mesozoic sediment deposits, Sweden	low	0·001–0·05%	[7]
Western Canada	low medium, high	<0·01% rarely >0·001%	[22], [24]
Cornwall, England	high	rarely >0·001%	[22], [24], [14]
Edwards, New York, U.S.A.	high	<0·01%	[22], [24]
New South Wales, Australia	high	<0·001%	[24]

Spectrographic investigations of blende specimens using the cathode layer carbon arc showed that in a number of blendes the gallium could not be wholly present as the antimonide, since spectra of specimens containing >0·02% Ga did not show the Sb line 2877·9 Å, although the minimum sensitivity of detection of the line by the method of analysis corresponds to 0·01% Sb. In the case of arsenic this type of argument is not admissible, since the minimum sensitivity of the As line 2349·8 Å corresponds to 0·1% As.

In order to gain information as to whether gallium can occur in blende in the absence of sufficient arsenic to form GaAs it was decided to investigate the co-precipitation of gallium with zinc sulphide.

When hydrogen sulphide is passed through a solution of a gallium salt, the hydroxide, not the sulphide, is precipitated, but if the solution is slightly acidified with a mineral acid, no precipitation can be observed. Experiment with radioactive Ga^{72} tracer, however, showed that when H_2S was passed through a solution

of gallium trichloride slightly acidified with hydrochloric acid, together with a zinc salt, some gallium was carried down in the resulting zinc sulphide precipitate.

This coprecipitation was investigated in a further experiment using inactive gallium, the resulting zinc sulphide precipitate being examined spectrographically. Hydrogen sulphide was passed at room temperature for 2 min through a slightly acid solution containing 0·1 g Ga^{3+} and 0·7 g Zn^{2+} per 100 ml. The resulting zinc sulphide precipitate was allowed to settle, and was then filtered and repeatedly washed with boiling water. The precipitate was dried, and the gallium content determined spectrographically.

The acidity of the solution employed in the experiment was such that no gallium precipitation would have been observed if no Zn^{2+} had been present.

Although the precipitated galliferous zinc sulphide was found to contain 0·21% Ga, no trace of arsenic could be detected in it spectrographically. At least some gallium can therefore be carried by zinc sulphide in a form other than as GaAs. This fact together with the evidence that arsenic could not be detected spectrographically in many quite gallium rich blendes, suggests that the idea of Goldschmidt and Peters that gallium occurs in blende as the arsenide is probably incorrect. A more definite proof of this point could be obtained by determining the arsenic content of blendes of known gallium content by a modification of the radioactivation method of analysis of Smales and Pate (1952).

The possibility that gallium occurs in blende in either the divalent or trivalent state linked to sulphur in place of zinc seems to provide a more likely explanation of the occurrence of gallium in blende.

Both GaS and Ga_2S_3 have been prepared in the dry way by Brukl and Ortner (1930) and Klemm and v. Vogel (1934), and x-ray powder photographs by Halla (Brukl and Ortner (1930)) have shown that they are different distinct species. Klemm and v. Vogel (1934) consider that GaS probably has a layer lattice, while Ga_2S_3 has been shown by Hahn and Klinger (1949) to have the blende structure ($a = 5{\cdot}17$ Å) below 550–600°C, and the wurtzite structure above that temperature.

Despite the fact that GaS, unlike Ga_2S_3, is unattacked by water and on Ahrens' (1953) ionic approach to mineral formation Ga^{2+} ions ($r = 0{\cdot}74$ Å, $I = 15{\cdot}93$ v) could quite reasonably substitute for Zn^{2+} ions ($r = 0{\cdot}74$ Å, $I = 18$ v), the close crystallographic similarity between Ga_2S_3 and ZnS certainly tends to suggest that gallium occurs in blende through trivalent gallium acting as proxy for zinc in the mineral lattice. The fact that GaS is diamagnetic (Klemm and v. Vogel (1934)) also provides evidence for this view, since if GaS contained divalent gallium it would probably be paramagnetic unless there was –Ga–Ga– linking, and this type of linking would be unlikely to occur in galliferous blende.

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The isotopic constitution of carbon in ancient rocks as an indicator of its biogenic or nonbiogenic origin

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ABSTRACT

The geologic and isotopic evidence serving to indicate the *biogenic* or *nonbiogenic* origin of carbon in rocks is discussed. A lower limit of the $^{12}C/^{13}C$ ratio of biogenic carbon is placed at 90·5. It is concluded that, in the absence of contradicting geologic evidence, carbon in shales, slates, and schists is biogenic if its isotopic constitution falls into the biogenic range.

Introduction

Nier and Gulbransen (1939) were the first to show that plants prefer to concentrate ^{12}C, the lighter of the two stable carbon isotopes, whereas the heavier isotope, ^{13}C, becomes concentrated in limestones. This difference in behavior is well defined and has been verified by numerous later investigations (e.g., Craig, 1953). On the basis of data available at that time, the writer (Rankama, 1948a, p. 411; 1948b, pp. 199, 203) related the variations in the isotopic constitution of carbon to the origin of carbon in the various geologic carbonaceous materials. Furthermore, he established the presence of two general groups of carbon, inorganic and organic, on the basis of isotopic constitution. Inasmuch as this division is not completely unambiguous, because any number of organic compounds may be synthesized that contain carbon exclusively composed of ^{13}C, it is proposed to call the general groups of carbon *nonbiogenic* and *biogenic* carbon. Inorganic and biologic processes are incapable of causing a complete isotopic fractionation of carbon, and in some instances a mixture of nonbiogenic and biogenic carbon may be present, e.g., in metamorphosed sediments that may contain graphite initially deposited as a weathering residuum, along with carbon of bituminous origin (Rankama, 1948b, p. 203).

Looking for conclusive evidence of the origin of carbon in pre-Cambrian metamorphic rocks, the writer (Rankama, 1948a), following a suggestion of Wickman (1941, p. 419) investigated the isotopic constitution in samples of native carbon from graphite deposits, coal, carbon-bearing schists, and the suggested fossil, *Corycium enigmaticum* Sederholm from eastern Fennoscandia. The carbon in the metamorphic derivatives of argillaceous sediments fell into the biogenic range, thereby producing independent information supporting the conclusion of many geologists, reached by applying the uniformitarian principle, that such carbonaceous rocks were originally bituminous or sapropelic sediments of biogenic origin.

The use of the isotopic constitution of carbon to indicate its biogenic or nonbiogenic origin in ancient rocks is based on several assumptions that may or may not be true. Thus, it is assumed that ancient organisms were able to fractionate the carbon isotopes in a way similar to that of their present-day counterparts. Furthermore, it is assumed that the isotopic constitution, once established, does

not materially change with changing physical and chemical conditions of the surroundings, i.e., remains rather unaffected by geologic processes. Finally, it is assumed that the isotopic constitution of carbon in the exchange reservoir has not materially changed during the geologic history of the Earth. The validity of these assumptions and the underlying geologic and chemical facts and principles will be discussed in the following sections.

Isotopic Fractionation of Carbon in Recent and Ancient Organisms

It is generally agreed that the first organisms to appear were aquatic plants. The isotopic constitution of plant carbon is known in rather great detail, but the isotopic constitution of animal carbon is still very inadequately known.

Ingerson (1953, p. 304) remarked that the isotopic fractionation or nonfractionation by extinct organisms can only be inferred by analogy with similar existing species unless a certain group or species always prefers a certain isotope, regardless of its geologic environment. In present-day plants, no systematic differences in the isotopic constitution of carbon have been observed. The gymnosperms that consistently contain somewhat less ^{12}C than do the other plants may, however, make an exception (Wickman, 1952, pp. 247, 251). Up to an age of more than 25,000 years, there is no correlation between the isotopic constitution of carbon in Pleistocene fossil wood and the age of the wood, and it also appears that the isotopic constitution of coal has not changed appreciably since the beginning of the Paleozoic (Craig, 1953, pp. 75–77). Craig also concluded that there is a good reason for the belief that the ancient marine plants and animals contained carbon with an isotopic constitution similar to that of the present-day marine vegetable and animal carbon. The writer is inclined to accept these conclusions. Because there is no fundamental dividing line at the outset of the Paleozoic, application of the uniformitarian principle extends Craig's conclusions with equal strength far back into the pre-Cambrian.

Changes in the Isotopic Constitution of Carbon Caused by Geologic Processes

Craig (1953, pp. 76, 77) found that alteration to coal has little effect on the isotopic constitution of carbon in wood. Furthermore, he concluded that there is no correlation between the isotopic constitution of carbon in coal and the degree of coalification. There appeared to be, however, some difference in the processes leading to the formation of coal and of petroleum, because petroleum carbon ends up with a greatly changed isotopic constitution and becomes very light. Craig also said that the black shales and carbonaceous schists which, in general, contain extremely light carbon may undergo an alteration similar to the alteration of petroleum. Craig's (1953, pp. 77, 78) data on the isotopic constitution of carbon in biogenic matter in a chalk from Palestine, contact metamorphosed by a basalt plug, indicate that the isotopic constitution of carbon does not change very much in contact metamorphism.

Wickman (1953) reached a similar conclusion after having studied an extensive material that consisted of three series of coal samples of Pliocene, Wealden, and Carboniferous age (see Table 2). It appeared from his results that a relatively

rapid thermal metamorphism does not affect the isotopic constitution of coal. In a similar manner, Mars (1951, pp. 137, 138) found that the isotopic constitution of coal graphitized at a high temperature in a smelting furnace did not undergo any decisive change. The results of Münther and Dansgaard (1951) indicated that graphitization of coal by a basaltic eruption did not change its isotopic constitution, while the carbon grew a little heavier in the graphitization of carbonaceous shales.

It appears from the foregoing results that direct thermal and contact metamorphism are not likely to cause material changes in the isotopic constitution of carbon. With reference to the effect of regional metamorphism, the situation is very incompletely investigated. The writer (Rankama, 1948a, p. 414; 1950, p. 77) felt that the conclusion is justified that carbon grows a little heavier, i.e. that ^{13}C is slightly concentrated in metamorphism and metasomatism (graphitization), and that differences in the degree of metamorphism may cause variations in the isotopic constitution of carbon in specimens from the same locality.

Definite proof of the metamorphic concentration of ^{13}C is still lacking and, in fact, may be very hard to produce. But it appears from isotopic analyses on graphite (Rankama, 1948a; Mars, 1951; Craig, 1953) that any enrichment of ^{13}C possibly caused by regional metamorphism cannot be very extensive.

Changes in the Isotopic Constitution of Carbon in the Exchange Reservoir

Mars (1951, p. 140), in searching for an explanation of some low $^{12}C/^{13}C$ ratios in graphite lenses found in certain pre-Cambrian gneisses of an assumedly sedimentary origin, raised the question whether such values could be assumed to reflect special conditions characteristic of the age and geologic setting of the said rocks. It seems to be possible to attribute such anomalies in the isotopic constitution, at least in part and for carbon of vegetable origin, to the characteristic differences between plants grown in different biotopes as observed by Wickman (1952). He found a pronounced difference between marine and terrestrial plants in general, the marine plants being heavier than the terrestrial plants. He related the observed differences to the intensity variations in the local carbon-dioxide cycle. Craig's (1953) work also showed a general effect of the biotope between marine and terrestrial plants, just like the one that Wickman observed. The explanation Craig gave, however, was entirely different from the one given by Wickman. Craig (1954) maintained the view that cyclic enrichment processes do not affect the isotopic constitution of carbon in the various groups of plants and that the enrichment of ^{12}C in normal terrestrial plants most probably is a result of the compounding of several fractionation stages within the plants. In the association of marine and some terrestrial plants with a liquid bicarbonate-carbonate phase or a solid carbonate phase Wickman (1953, p. 253) and Craig (1953, p. 74; 1954) found support for the opinion that partial derivation of carbon from the carbonate phase is responsible for the higher ^{13}C content of the said plants, as compared with terrestrial plants in general. These mechanisms, even though possibly not correct in all details, as Craig said, nevertheless appear very acceptable.

Furthermore, the carbon in a plant is not necessarily of constant isotopic

constitution throughout the species, and slight variations in the same plant species from different localities also occur that may or may not be caused by local differences in the isotopic constitution of carbon in atmospheric carbon dioxide, as Craig (1953, pp. 68–70; 1954) maintained. Differences in the isotopic constitution of carbon in different plant species from a given locality indicate that certain variable factors in individual plants affect the isotopic constitution of plant carbon (Craig, 1954). This vital effect probably corresponds to the organism effect that, according to Craig (1953, pp. 61, 62) determines the isotopic constitution of carbon in the carbonates deposited by marine animals.

It appears from the foregoing discussion that the isotopic constitution of carbon in the exchange reservoir affects the isotopic constitution of plant carbon. Wickman (1952, p. 352) remarked that this situation somewhat modifies the possibility of investigating the history of early life. But, as he said, if it is correct to assume that life was first created in stagnant water, then there is a fairly good chance of tracing life far back into the pre-Cambrian. The possible age effect, i.e., the increase in the $^{12}C/^{13}C$ ratio in coal with decreasing age independent of the degree of coalification (see Table 2), still does not allow any conclusions relative to a possible variation with time of the isotopic constitution of carbon in atmospheric carbon dioxide (Wickman, 1953, pp. 249, 250).

Isotopic Constitution of Plant Carbon in Various Biotopes

Wickman (1952) and Craig (1953) published collections of isotopic analyses of plant carbon. These data are grouped in Table 1. The lower limit, given parenthetically, of the terrestrial plants refers to the anomalous species from deserts where the cycle of carbon dioxide cannot develop (Wickman, 1952, p. 253) and to those deriving a part of their carbon from calcium carbonate in the substratum (Craig, 1953, p. 70). The remaining values indicate a rather pronounced difference between the normal terrestrial range and the marine range and emphasize the

Table 1. *Isotopic constitution of plant carbon*

Group of plants	$^{12}C/^{13}C$ range*	*Reference*
Terrestrial (all)	(89·63) 90·49–91·43	Wickman (1952)
Terrestrial (all)	(89·99) 90·94–91·55	Craig (1953)
Marine	89·19–90·30	Wickman (1952)
Marine	89·62–90·43	Craig (1953)
Limnetic (all)	89·25–91·16	Wickman (1952)
Limnetic (all)	90·11–90·95	Craig (1953)
Limnetic (stagnant)	90·85–91·16	Wickman (1952)

* Craig's values, recalculated as $^{12}C/^{13}C$ ratios, are based on the $^{12}C/^{13}C$ ratio of 88·89 in a secondary standard; Wickman's value for the same standard is 88·68 (Craig, 1954). The systematic difference, 0·21, between the two sets of data does not affect the considerations presented in the discussion of Table 1.

effect of dissolved bicarbonate and carbonate as a carbon source of marine plants. It may be noted in passing that the marine invertebrates with a $^{12}C/^{13}C$ range from 89·85 to 90·51 in their organic carbon (Craig, 1953, p. 62) make a similar instance. Also, limnetic plants appear to derive some of their carbon from the bicarbonate and carbonate ions. Wickman's results indicate that limnetic plants in general stretch from the lower marine range to the higher end of the normal terrestrial plant range. Craig's values are derived from only three analyses and roughly cover the range between marine and terrestrial plants. Wickman's range for limnetic plants living in stagnant water encircles rather closely the $^{12}C/^{13}C$ ratio of 91.

Craig (1954) believed that stagnant water as such does not necessarily cause enrichment of ^{12}C but that rate and source of supply of carbon dioxide (e.g., from decaying biogenic matter such as land-plant litter) are important factors.

Isotopic Constitution of Carbon in Fossil Wood and Coal

The pertinent information is assembled in Table 2, compiled from data published by Craig (1953) and Wickman (1953). Tables 1 and 2 indicate that fossilized plant carbon lies well within the range of carbon from recent terrestrial plants. The youngest, Pliocene, coals analyzed by Wickman fall into the range of carbon from fresh-water plants growing in stagnant water, but the older coals diverge from the said range, the more the higher their age.

Table 2. Isotopic constitution of carbon in fossil wood and coal

Material	$^{12}C/^{13}C$ *range**	*Reference*
Fossil wood	91·10–91·20	Craig (1953)
Peat, lignite, coal, anthracite	90·85–91·38	Craig (1953)
Pliocene coals, Sumatra	90·87–91·10	Wickman (1953)
Wealden coals, Lower Saxony	90·53–90·98	Wickman (1953)
Carboniferous coals, Rhine province	90·51–90·89	Wickman (1953)

* See footnote on p. 145

Isotopic Constitution of Carbon in Argillaceous Sedimentary and Metamorphic Rocks

Table 3 gives the ranges of the $^{12}C/^{13}C$ ratios for shales, slates, and schists of argillaceous origin of varying age, compiled from various sources and made commensurable by means of referring them to the so-called Stockholm carbon standard ($BaCO_3$; see Wickman, Blix, and von Ubisch, 1951, p. 143). Tables 1 and 3 show that also in the argillaceous rocks carbon checks rather closely with carbon from both terrestrial plants and limnetic plants growing in stagnant water.

Craig (1953, pp. 78–81) remarked that there is a striking similarity in the isotopic constitution of carbon in black shales, oil shales, and petroleum that may be a result of similar conditions of deposition. He suggested that the lightness

of carbon in these deposits is a result of the concentration of compounds containing very light carbon, such as waxes, fats, and oils, in the source material. Because this concentration does not take place during the formation of coal, carbon in coal will inherently be somewhat heavier. These conclusions appear plausible in the light of geologic and geochemical evidence.

Table 3. Isotopic constitution of carbon in shales and schists (Ranges in parentheses are based on the Stockholm carbon standard)

Material	$^{12}C/^{13}C$ *range*	*Reference*
Cenozoic, Mesozoic, and Paleozoic shales and slates	90·52–91·71 (90·31–91·50)	Craig (1953)
Paleozoic schists	90·87–91·13 (90·66–90·92)	Craig (1953)
Pre-Cambrian schists	89·77–92·16 (89·56–91·95)	Craig (1953)
Pre-Cambrian schists (Finland)	90·2–92·0* (89·8–91·6)	Rankama (1948a)
Pre-Cambrian schists (Sweden)	91·0; 91·5* (90·6; 91·1)	Mars (1951)
Pre-Cambrian schists (S.E. Manitoba)	(90·06–90·86)	Rankama (1954)

* The original results are directly comparable to those of Murphey (1941) who gave a $^{12}C/^{13}C$ ratio of 89·2 for the Jurassic limestone from Solenhofen, Bavaria. Re-examination of this rock gave a primary standard with a ratio of 88·97 (Nier, 1950, p. 793). Because Craig's values are higher by 0·21 than Wickman's values (see footnote on p. 145), and because Craig's secondary standard is based on Nier's remeasured primary standard, 0·2 is deduced from the originally measured ratios to make them commensurate with those based on the Stockholm standard. In addition, 0·2 is deduced to bring the values down to the level of the new measurement of the primary standard.

Geologic Theory of the Origin of Carbon in Ancient Metamorphosed Argillaceous Sediments

It is a generally adopted belief among geologists that the graphite- and pyrite-bearing slates, schists, and graywackes found in the pre-Cambrian formations are of bituminous and sapropelic origin (Eskola, 1932, pp. 27–28; 1938, p. 347; Hausen, 1943, pp. 17–19; Pettijohn, 1943, p. 948; 1949, p. 459; the views are summarized in Rankama, 1948a), It is believed that such rocks originally were subaquatic sediments formed, in the presence of organisms, in the same way as bituminous and sapropelic sediments are known to form still today. This conclusion rests on the uniformitarian principle that, according to all evidence gathered in different parts of the world, has not lost its validity even in the oldest rocks so far encountered. Geologists are eager to admit, however, that this conclusion of

the biogenic origin of carbon in the very ancient argillaceous rocks is not completely safe, inasmuch as it is valid only as long as the uniformitarian principle is valid. But it is supported by observation. Thus, the occurrence of the carbonaceous substance as a cement between the mineral constituents of the nearly always relatively fine-grained argillaceous rocks strongly suggests its presence as a primary constituent in the original sediment. Primary sedimentary structures and actual argillaceous composition even in the most ancient carbon- and sulphide-bearing schists, and their similarity to the bituminous and sapropelic shales of Paleozoic and later age strongly suggest an identical origin.

The conclusion follows that there are no geologic reasons contradicting the assumption of a biogenic origin for carbon in even the oldest known pre-Cambrian argillaceous carbon-bearing slates, schists, and graywackes.

Isotope Chemical Aspects of the Validity of the Geologic Theory

Wickman and v. Ubisch (1951, pp. 120, 121) pointed out that, in principle, there are four possible sources of carbon in rocks, viz. biogenic matter, carbonates reduced by rock melts, reduced magmatic carbon monoxide and carbon dioxide, and any combination of these sources. They felt that in some instances it is possible to characterize a source by means of the isotopic constitution of carbon derived therefrom. Thus, for biogenic matter the $^{12}C/^{13}C$ ratio is greater than 91·0, and for limestones it is less than 90·0. For magmatic carbon they assumed a tentative range from 89·0 to 91·5. Data presented in Tables 1 and 2 indicate that a reasonably safe lower limit of the biogenic range may be placed at 90·5. Because of the existence of variations in the isotopic constitution of carbon in plants, even in a single species, and because of the possibility that changes are produced by regional metamorphism in the isotopic constitution of carbon, a dynamic reasoning must be applied, as always when dealing with geologic material, and in a series of $^{12}C/^{13}C$ ratios measured with comparable analytical errors the highest observed ratio should be the significant and decisive one (Rankama, 1950, p. 77).

The lower limit of 90·5 for the $^{12}C/^{13}C$ ratio of biogenic carbon is based on the measurements of Wickman (1952, 1953). He used a technique that is known to involve a possible source of error (Baertschi, 1952; Craig, 1953). Craig's data quoted in Table 1 and obtained by a faultless method are essentially identical with Wickman's values, as Craig (1954) himself remarked, and consequently the errors produced by the method that Wickman used evidently tend to be insignificant. Another source of error is the difference in the abundance of ^{17}O between the sample and the standard (Dansgaard, 1953), but also in this instance the errors caused in the measured isotopic data probably are small.

Biogenic origin of carbon in geologic materials has been deduced from isotopic constitution in two instances. The writer (Rankama, 1948a) concluded that carbon in several pre-Cambrian schists of argillaceous origin in Finland is biogenic. Münther and Dansgaard (1951) investigated the origin of graphite-bearing basalts of Disko Island in West Greenland. These basalts contain numerous inclusions of carbonaceous shale from underlying strata, coal interbedded between

the thin flows, and graphite in great abundance. The $^{12}C/^{13}C$ ratios (90·5–90·8 in prebasaltic shale, 91·5 in shale inclusions, 91·1 in interbasaltic coal, and 91·2 in graphite from basalt) were interpreted to prove the biogenic origin of the graphite. This is, geologically, an unobjectionable instance, because on Disko Island the whole sequence from shale to graphite actually can be followed.

Craig (1953, pp. 59, 83–85) strongly disputed such interpretations claiming that they suffer from a serious handicap imposed by one's inability to calculate the equilibrium constants for isotope exchange between graphite and other carbonaceous compounds. Therefore, he felt that it is impossible to determine the origin of graphite from its isotopic constitution. Furthermore, he criticized the statement of Wickman and v. Ubisch (1951, p. 121) that if the graphite in a limestone is derived from carbon dioxide released from the carbonate, it is likely that its isotopic constitution is very much similar to the constitution of carbon in the carbonate, while if it is derived from biogenic carbon its isotopic constitution should differ greatly from that of the carbonate carbon.

Craig said that there is insufficient chemical evidence to justify such conclusions. There being graphites that are even lighter than plant carbon he concluded that the isotopic constitution of carbon in such graphites, if of biogenic origin, has changed in the same way as it has changed in black shales and in petroleum, unless the isotopic constitution of surface carbon has changed in the course of geologic evolution. But Craig's (1953, p. 77) own data indicated $^{12}C/^{13}C$ ratios as high as 91·71 in sedimentary biogenic carbon, and he also concluded that the isotopic constitution of surface carbon has not changed appreciably since the Paleozoic. Next, Craig considered the tacitly made assumption that it is impossible to derive light graphite from heavy carbonate, and heavy graphite from light biogenic carbon in the various isotope-exchange equilibria between graphite and other carbonaceous compounds. He said that it is impossible to make such an assumption unless the fractionation factors between graphite and the other carbonaceous compounds are known at the temperatures postulated for the formation of graphite. Furthermore, the compounds involved in the making of graphite are unknown, and there is no assurance that the processes took place under equilibrium conditions. To all this one may say that there certainly exists no positive evidence, geologic or other, indicating that a graphite deposit, or graphite disseminated in a schist, was formed under equilibrium conditions. Consequently, application of isotope-exchange equilibria to a discussion of graphite formation is groundless and offers no help. The tacit assumption relative to the formation of light and heavy graphite consequently cannot be disqualified. The available evidence indicates that light carbon does not grow heavier during graphitization (Münther and Dansgaard, 1951).

In a further attempt to apply equilibrium theories to natural phenomena, Craig considered the formation of graphite from carbon dioxide by dissociation or reduction. He found the decomposition of carbon dioxide difficult to understand, inasmuch as the equilibrium constants for the various possible reactions indicated that carbon dioxide is stable over the whole range of metamorphic temperatures, unless some reducing element is present. It so happens that the formation of graphite by reduction from carbon dioxide has been observed and

investigated (Frauenfelder, 1924; reference was made to this work and to supporting field evidence in a previous paper of the writer: Rankama, 1948a, p. 394). Frauenfelder passed carbon dioxide through a silica tube at approximately 1 100°C and from 2 atm. to 3 atm. pressure and observed the formation of graphite crystals on the inner and outer surfaces of the tube, in particular, at the colder (700° – 800°C) parts. To make sure that the graphite was not formed by the reactions

$$2CO_2 \rightarrow 2CO + O_2; \qquad 2CO \rightarrow 2C + O_2$$

Frauenfelder burned graphite in a stream of oxygen (in excess) in the silica tube heated at 1 100°C. Graphite crystals were obtained also in this experiment. Frauenfelder ascribed the formation of graphite to the action of silica as a catalyst.

It is not too difficult to visualize the formation of graphite at igneous contacts in limestone bodies by the reduction of carbon dioxide. With all due respect to the dissociation constants introduced by Craig, it appears that one has here another case in point to indicate that Nature does not always obey the rules set up for her guidance in the laboratory.

Conclusions

It appears from the foregoing discussion that the conclusions relative to the biogenic origin of carbon in metamorphic schists cannot be disqualified by resorting to isotope chemical data obtained by laboratory experiments. The geologic setting of the samples must always be considered with an open mind. Of course, it is not always possible to decide whether the carbon in a rock is of biogenic origin or not. Thus, e.g., carbon in a number of igneous rocks investigated by Craig (1953, pp. 80, 81) lay generally in the biogenic range. In an igneous rock, this is no proof of the derivation of carbon by biogenic contamination unless, as in the instance of the Disko Island basalt, there is conclusive geologic evidence indicating the origin. In the absence of contradictory geologic evidence, one is safe to conclude that finely disseminated carbon in shales, slates, and schists, and the carbonaceous accumulations in these rocks, are of biogenic origin if their isotopic constitution lies within the biogenic range. This conclusion refers to such rocks irrespective of their age. Low values for the $^{12}C/^{13}C$ ratio in sapropelic rocks may result from contamination of the source material by terrestrial plant remains. If geologic evidence is positive one may also consider a biogenic origin in such rocks for carbon that is somewhat heavier than biogenic carbon. This conclusion rests on the observed lower $^{12}C/^{13}C$ ratios in plants obtaining a part of their carbon dioxide supply from bicarbonate and carbonate. Presence of supporting geologic evidence also validates a biogenic origin for the lightest carbons in the rocks considered, because it appears that the type of the original biogenic matter affects the isotopic constitution of carbon in the carbonaceous compounds that are derived therefrom.

With reference to the most ancient pre-Cambrian carbonaceous slates and schists investigated, viz., those from Finland and Manitoba, one should, perhaps, consider that life was approximately 1·5 and 2·5 billion years, respectively, younger

at the time their original matter was laid down than today. It may be possible that biologic processes at that time were unable to produce as thoroughgoing a fractionation of the carbon isotopes as do their present-day counterparts. Another hypothetical possibility is that the isotopic constitution of carbon in atmospheric carbon dioxide and in surface carbon before the start of biologic processes was different from its present-day constitution.

The Earth is changeable, not constant, and the time factor affects geological processes. There is a profound difference between the closed systems investigated in a laboratory and the open systems, generally devoid of equilibrium, that exist in Nature. Consequently, when dealing with geologic material, one should be hesitant in accepting conclusions that rest solely on chemical theory and evidence. The importance of geologic viewpoints is adequately illustrated by a statement of INGERSON (1953, p. 361), viz., that predictions relative to expected isotopic fractionation by natural processes involving exchange reactions at equilibrium, among other things, should be based on equilibria representing reactions that are probably operative, or at least approximated, in natural processes. With these remarks in mind, one is greatly relieved to read the recent statements of CRAIG (1954) that it appears more likely that the distribution of ^{12}C and ^{13}C between marine plants and precipitated carbonate during the utilization of carbon dioxide derived from bicarbonate actually is governed by kinetic factors and rates of mixing, rather than by isotopic equilibrium conditions between carbon dioxide and carbonate; that methods used in the laboratory for kinetic experiments with ^{13}C and ^{14}C are known to introduce some variable which does not affect plants in Nature and that, consequently, one should not attempt to apply such results to the study of natural systems; and, finally, that even though the chemist can propose physical and chemical mechanisms that may produce certain effects, it will remain the task of the geologist to evaluate the degree to which the proposed mechanisms may have operated in Nature.

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NOTICE

METEORITICS

The Journal of the Meteoritical Society and the Institute of Meteoritics of the University of New Mexico

From the time of the inception of the Meteoritical Society in 1933, its *Notes and Contributions* were published regularly in the monthly magazine, *Popular Astronomy*, until December, 1951, when that periodical was discontinued on the completion of its 59th volume. By arrangement with the University of New Mexico a new publication entitled *Meteoritics: The Journal of the Meteoritical Society and the Institute of Meteoritics of the University of New Mexico* was established, and its premier issue, consisting of 25 items and 123 pages, appeared in December, 1953.

Meteoritics is to be issued at least once but not more than four times a year. It is expected that eventually the journal will become a quarterly. Dr. FREDERICK C. LEONARD of the University of California, Los Angeles, is the Editor, and the Director of the Institute of Meteoritics of the University of New Mexico, Dr. LINCOLN LAPAZ, is the Associate Editor. The annual subscription price to both members and non-members of the Meteoritical Society, is $4.00 (or, to student members, $2.00), regardless of the number of issues published. Orders for subscriptions should be sent to the Secretary of the Meteoritical Society, Dr. John A. Russell, Department of Astronomy, University of Southern California, Los Angeles 7, California.

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